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THE SARNIA OXIDANTS STUDY (JUNE 27-JULY 18, 1984):

Analysis of the Air Quality and Meteorological Data

Report ARB-124-85-AQM

Ministry
of the
Environment
Ontario

Dr. David Balsillie, Director
Air Resources Branch

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Analysis of
The Air Quality and Meteorological Data

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Summary

During the period June 27 - July 18, 1984, an intensive field study was carried out in the Sarnia area of Ontario, with the following primary objectives:

(i) to determine the contribution to ozone levels in southwestern Ontario caused by hydrocarbon and nitrogen oxide precursor emissions at Sarnia; and

(ii) to determine the meteorological conditions under which the Sarnia contribution makes up an important portion of the total ozone levels in southwestern Ontario.

The regular air quality and meteorology monitoring network was supplemented with additional measurements for the study period, and an instrumented aircraft was used to assist in the mapping of ozone and other important species in the study area.

The main conclusions of this study are:

(i) Oxidant precursor emissions from the Sarnia area can lead to the formation of elevated ozone levels downwind. On the basis of the results obtained during the study period, a measurable Sarnia impact would be expected to occur about 30% of the time during the summer months, on sunny days, especially with low wind speeds and inhibited atmospheric mixing.

(ii) On these occasions, maximum ozone buildups (above regional background levels) up to about 20-40 ppb can be expected. The affected areas can be on the order of 100-1000 km^2 in size, and the duration of the impact - several hours. At times, the Sarnia contribution to the total oxidant levels can push hourly ozone concentrations over the provincial air quality criterion of 80 ppb.

(iii) Nevertheless, judging from the frequency of occurrence of ozone buildups attributable to Sarnia emissions, the size of the area

affected (on the order of 1% of the total area of southern Ontario, where exceedences of the provincial air quality criterion of ozone are frequently observed), and the magnitude of the Sarnia contribution compared to regional background values, it is clear that ozone levels in southwestern Ontario in the summer are largely governed by the imported component, rather than ozone generation from local emissions.

The above conclusions are based on a relatively small data set, which may not be entirely representative of the long-term situation, but they seem to be consistent with the findings of other investigators who have studied the formation of ozone downwind of urban and industrial areas. Also, the findings of this study will be supplemented by a meteorological analysis of the long-term air monitoring data in the Sarnia area, as well as a mathematical modelling study of the impact of the Sarnia emissions on regional ozone levels, both of which are currently underway as part of Ontario's oxidant control strategy development.

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1. Introduction

Ontario's air quality criterion for ozone (0.08 ppm hourly average) is frequently exceeded during the growing season (June, July and August) in southwestern Ontario. It has been estimated that, if control efforts could succeed in meeting the above criterion in all sections of the province, farmers would benefit by up to $23 million a year in extra production of various agricultural crops, such as tobacco, soybeans, wheat and white beans (Linzon et al., 1984).

A number of studies have examined the meteorological conditions accompanying ozone episodes in southern Ontario (Mukammal, 1965; Yap and Chung, 1977; Chung, 1977; Anlauf et al., 1977; Shenfeld et al., 1978; Mukammal et al.; 1982; Heidorn and Yap, 1984). It has been found that elevated ozone levels commonly occur over widespread areas during the spring and summer, typically on the rear sides of anti-cyclones or in the warm sectors of cyclones. While long-range transport from the northeastern United States is strongly implicated as the cause of ozone concentrations during these conditions, there is also evidence of ozone formation from local emissions in southern Ontario. Figure 1, for example (Shenfeld et al., 1978), shows ozone "bulges" around the Metropolitan Toronto and Windsor - Sarnia areas during episode days in 1978, which are most probably due to locally emitted ozone precursors.

The existence of such "bulges" around significant hydrocarbon and nitrogen oxide source areas is to be expected, in view of a number of field studies which have shown buildups of ozone a few hours downwind of urban and industrial areas of various types (see, for example, Westberg et al., 1981; van Duuren et al., 1981; Neuber et al., 1981; Spicer et al., 1982; Sexton, 1983; Sexton and Westberg, 1983a and 1983b). The Sarnia area, with its concentration of petrochemical industries, was thus of considerable interest, because of both its location in a portion of Ontario which is already subject to heavy ozone loadings due to long-range transport from the south, and its role as an important emitter of hydrocarbons and nitrogen oxides. Figure 2, for example, shows the location (by grid square) and annual anthropogenic emission rate in the Sarnia area for nitrogen oxides and various hydrocarbon species. The alkenes and alkyl benzenes, which are known to be efficient ozone precursors, have been broken out in a separate column in Figure 2. A similar procedure has been used for benzene and the low molecular weight alkanes, which are poor ozone precursors.

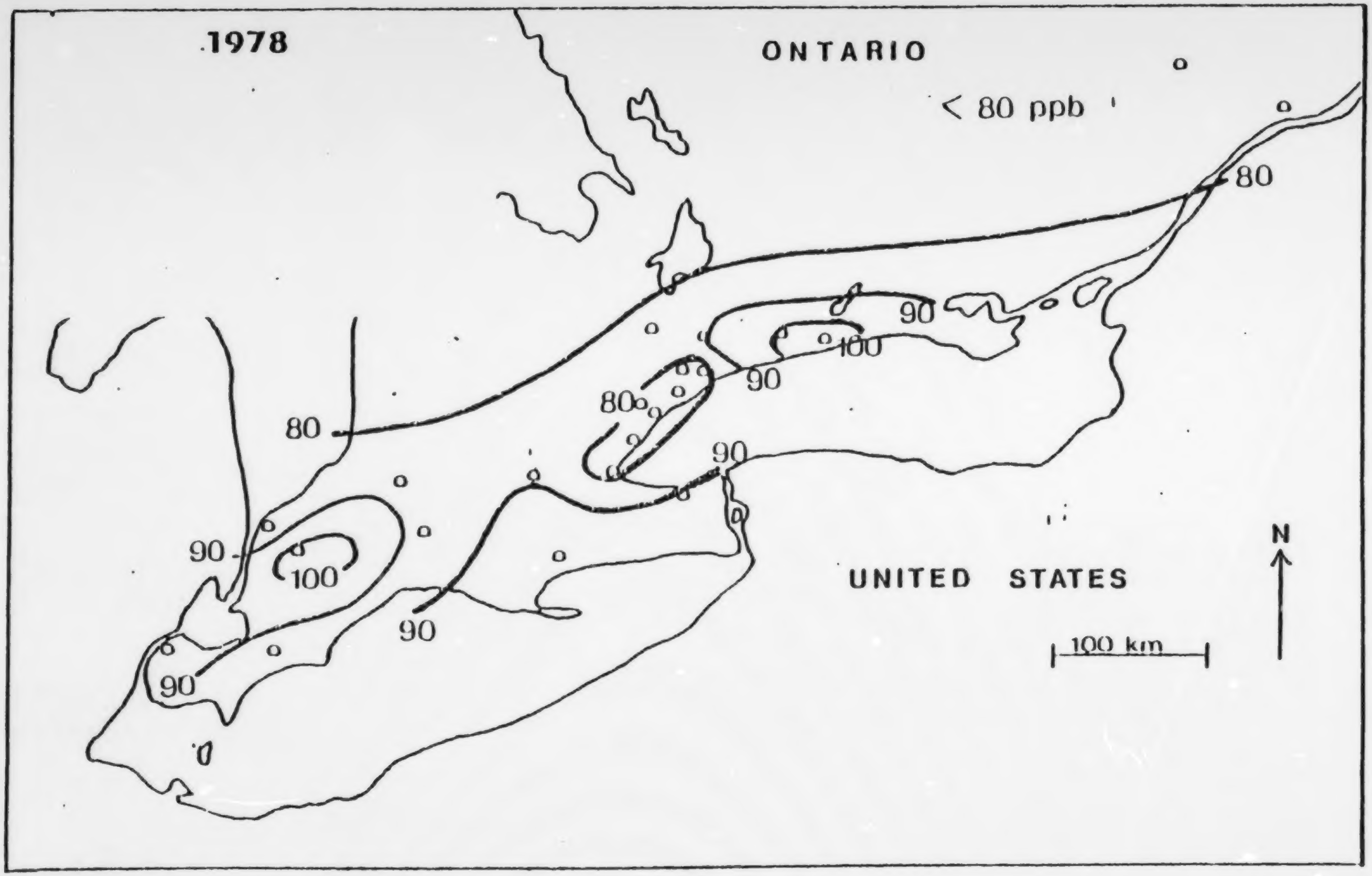
Accordingly the Sarnia Oxidants Study was carried out by the Air Resources Branch of the Ontario Ministry of the Environment (MOE), at the request of the Ministry's Southwestern Region. Environment Canada, Lambton Industrial Society and York University also participated. The study was part of Ontario's Oxidant Control Strategy Development, and had the following objectives:

(i) to determine how much ozone, over and above "background" levels imported into the area, is contributed by precursor emissions from Sarnia itself;

(ii) to determine under what meteorological conditions Sarnia contributions make up an important portion of the total ozone levels in southwestern Ontario, as compared to long-range transport; and

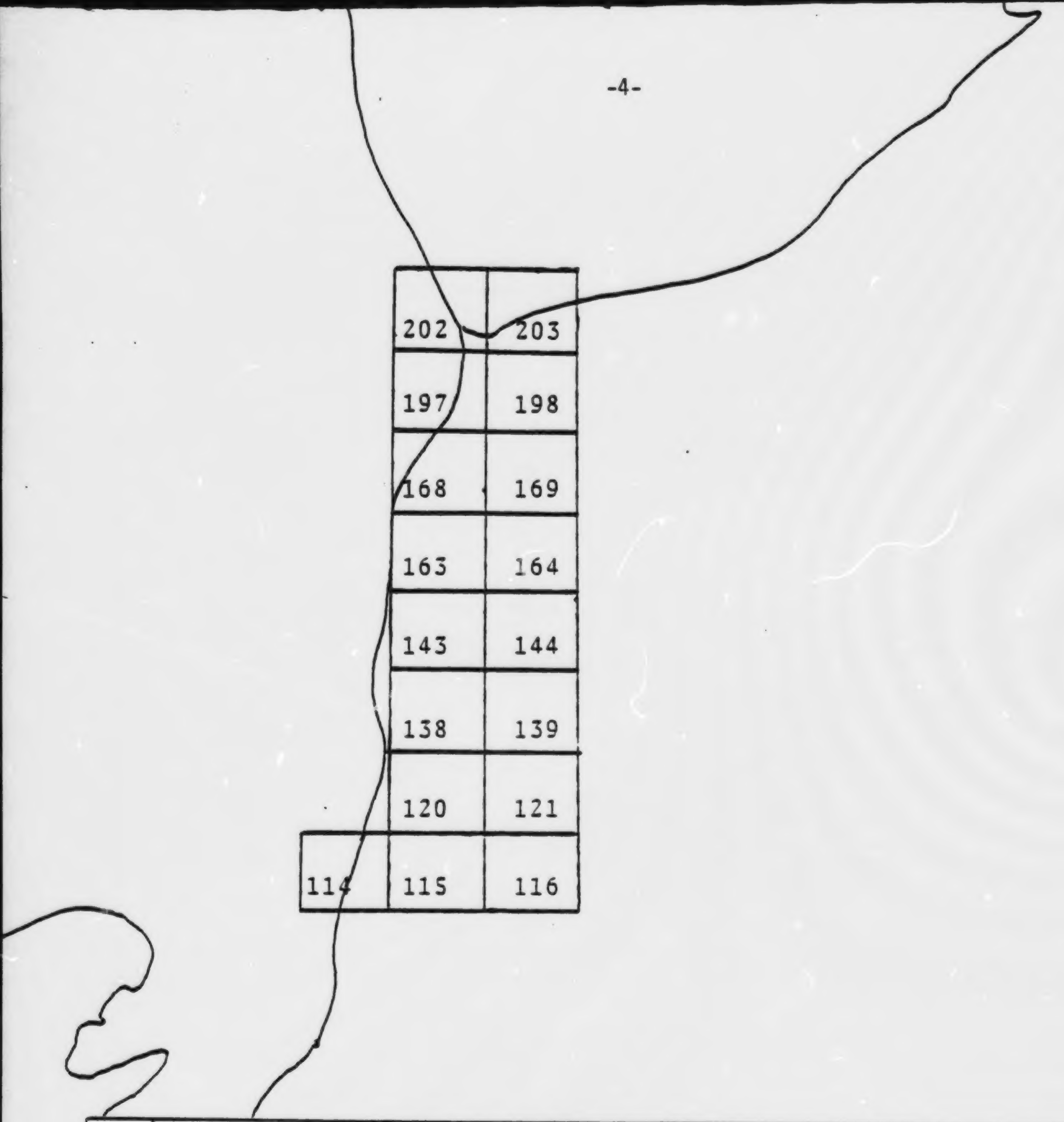
(iii) to determine which precursor (NO_x or hydrocarbons) should be controlled in order to lower oxidant levels in the Sarnia area.

During the period June 27 - July 18, 1984, extensive measurements were made of ozone and ozone precursors, using supplementary ground - based monitors (in addition to the regular air monitoring network) and an instrumented aircraft. The existing meteorological network was also enhanced with acoustic sounder and minisonde measurements. The details on monitoring techniques and observations from these individual measurement programs are reported in a number of Ontario Ministry of the Environment reports (see Ministry of the Environment, 1985), as well as by Hastie and Schiff (1984). The present report contains an analysis of the data directed towards objectives (i) and (ii) above, i.e. what is the Sarnia contribution toward oxidant levels in southwestern Ontario?; and, under what conditions is this contribution important? The third objective will be addressed in a separate report.



1978
ONTARIO
< 80 ppb
80
80
90
100
90
80
90
90
100
90
90
UNITED STATES
N
100 km

Figure 1: Average Ozone Maxima for 43 Episodes in 1978 (Shenfeld et al., 1978)



No.	EMISSIONS (METRIC TONS PER YEAR)						
	C_2-C_3 Alkanes & Benzene	> C_3 Alkanes	Alkenes		Alkyl Benzenes	Alkyl Benzenes & ≥ C_2 Alkenes	NO_x
			Ethylene	Others			
114	2.38	14.70	3.70	5.61	7.59	13.20	11.60
115	1.90	8.83	6.26	1.43	3.06	4.49	8.97
116	1.90	8.83	6.26	1.43	3.06	4.49	8.97
120	3.81	21.32	8.41	6.68	9.89	16.57	10.26
121	2.13	9.93	7.04	1.59	3.44	5.03	10.09
138	116.72	264.42	14.26	8.01	11.92	19.93	19714.02
139	3.54	17.28	12.89	2.93	5.47	8.40	20.76
143	5.73	31.13	16.11	8.42	12.68	21.10	27.71
144	4.05	19.72	14.74	3.34	6.23	9.57	23.72
163	814.76	1976.64	86.71	802.79	570.92	1373.71	20.92
164	4.05	19.72	14.74	3.34	6.23	9.57	23.72
168	1448.57	2507.27	3035.79	18225.59	2872.97	21098.56	13838.20
169	12.10	60.04	46.26	10.51	18.15	28.66	77.81
197	760.84	3672.14	100.63	109.50	1036.00	1145.50	10244.10
198	65.05	797.70	595.57	184.99	299.43	484.42	1570.00
202	19.27	142.73	97.33	34.26	52.05	86.31	220.66
203	25.29	284.46	207.25	68.26	106.52	174.78	1491.00

Figure 2: Hydrocarbon and NO_x Emissions in the Sarnia Area (by 5 km grid square)

2. The Measurement Program

During the Sarnia Oxidants Study, an extensive data set was collected both on the ground and aloft. In addition to the pollutants monitored routinely (O_3, NO and NO_x, SO_2, CO, hydrocarbons) at a number of Ministry of the Environment Stations, several specialized air quality measurements were made. These included:

(i) Hydrocarbon speciation of samples collected (as hourly averages) by the MOE mobile laboratories MAMU #1 and #2 at Courtright and Camlachie, as well as on the aircraft (as 15 or 30 minute averages) during flights upwind and downwind of Sarnia. Additional hydrocarbon samples were collected by the Environmental Protection Service (EPS) of Environment Canada at Courtright, on Tenax and Ambersorb cartridges, for subsequent analysis at the EPS Ottawa Laboratory. However, because of various problems, only five of these samples could be analysed. Therefore the EPS results have not been included in the present report.

(ii) Measurements of aldhydes, ketones, acetates and alcohols: formaldehyde was monitored at Camlachie by the York University group using their tunable diode laser spectrometer (TDLAS). The other compounds were monitored at Courtright, using MOE's trace atmospheric gas analyser (TAGA).

(iii) Measurements of some other parameters indicative of photochemical activity in the air mass: these included hydrogen peroxide (by TDLAS at Camlachie); and light-scattering particulates, sulfates and nitric acid (in the aircraft).

(iv) High-sensitivity measurements of NO and NO_x at Camlachie, using a modified chemiluminescent analyser developed by York University with the support of a MOE grant. Since the commercially available NO_x instruments used at other monitoring locations in the Sarnia area have relatively poor detection limits, it was hoped that this ultra-sensitive analyser would supply important information on the NO_x levels. Unfortunately, due to operational problems, only a partial data set was collected.

(v) Ozone precursor measurements: the ozone precursor monitor has been described by Belanger and Ortman (1984). Two such instruments were deployed, at Courtright and Camlachie, where concurrent measurements were being carried out on nitrogen oxides and hydrocarbons. Basically, the ozone precusor monitors are reaction chambers where the ozone content is measured before and after artificial irradiation (with u.v. lamps) of an ambient air sample. It was hoped that an analysis of the ozone levels before and after irradiation, together with the concurrent NO_x and hydrocarbon monitoring results, would give information on which precursor species contributes most to ozone levels in the Sarnia area.

The meteorological measurements collected by the regular towers were also supplemented, notably by an acoustic sounder to measure atmospheric stability (at Petrolia) and by two minisonde stations (at Petrolia and Camlachie) to measure wind speed and temperature as a function of height.

Figure 3 shows the location of monitoring sites which provided data for this study. The air quality and meteorological measurements made at each location (as well as on the aircraft) are summarized in Tables 1 and 2. For the oxidant-related parameters (O_3, NO_x and hydrocarbons, plus some of the aldehydes and ketones which are found in photochemical smog), an overview of the air quality data available during the study period is shown in Table 3. For data on other pollutants, see reports MOE/ARB-021-85-ARSP and MOE/ARB-020-85-ARSP.

For details of the monitoring techniques used, the reader is referred to the following reports:

(i) The airborne measurements - MOE/ARB-019-85-ARSP.

(ii) The MOE mobile laboratories at Camlachie and Courtright - MOE/ARB-021-85-ARSP.

(iii) The meteorological measurements - MOE/ARB-023-85-AQM.

At the fixed monitoring sites, O_3 and NO_x were monitored using chemiluminescent analysers; hydrocarbons, with flame ionization detectors; sulfur dioxide, by pulsed-florescence techniques; and carbon monoxide, using infra-red absorption.

It should also be noted that, at the beginning and toward the end of the study period, all O_3, NO_x and hydrocarbon analysers in the Sarnia area which were involved in the study were audited by the Ministry's Instrumentation Unit, thus ensuring comparability of the results.

The Sarnia Oxidants Study was designed to take maximum advantage of the air quality mapping capabilities of the aircraft. A tradeoff had to be made between spatial coverage and vertical resolution, since only one aircraft was available, with an endurance of about 5 hours. We chose the former. Since the principal objective of this study was to identify the effect of the Sarnia petrochemical complex on ozone levels in southwestern Ontario, most of the aircraft sampling consisted of crosswind transects, within the mixing layer at various distances downwind of Sarnia. However, upwind transects were also carried out, to establish the background levels. On some occasions spirals were flown, to determine the vertical pollutant structure. There were also some other deviations from this procedure. For example, on July 8, when winds were light and variable, samples were collected over the Sarnia area itself, in order to get a measure of ozone, hydrocarbon and nitrogen oxide concentrations in air parcels freshly exposed to Sarnia emissions.

A total of fourteen flights, each lasting typically for two to four hours, were carried out during the study period. During the flight days, minisondes were released (every hour or every two hours, depending on the meteorological conditions on the day in question) and hydrocarbon samples were collected for speciation by gas chromatography. Radio contact was maintained between the base station at Sarnia airport, the MAMU units at Courtright and Camlachie, the minisonde crew at Petrolia, and the aircraft, so that information updates on meteorological and ground-level air quality conditions could be relayed to the aircraft. In this way it was possible to alter if necessary the flight plans which had been formulated in the morning, in consultation with the Sarnia airport weather office, and thus optimize the usefulness of the collected data.

Table 1
Summary of Air Quality Measurement Made at Each Monitoring Station and on Aircraft

1.*	Windsor	O_3, $NO/NO_2/NO_x$, THC[1], RHC[2], SO_2, CO, COH[3]
2.	Merlin	O_3
3.	Bickford	SO_2
4.	Courtright	O_3, $NO/NO_2/NO_x$, THC, RHC, SO_2, CO, H_2S, selected aldehydes, ketones acetates, alcohols, hydrocarbons by gas chromatography, ozone precursor monitor
5.	Sixth Line	RHC, C_2H_4, SO_2
6.	River Bend	O_3, NO/NO_2, RHC, C_2H_4, SO_2
7.	LaSalle Road	RHC
8.	Scott Road	RHC
10.	Front Street	O_3, NO/NO_2, SO_2
11.	Centennial Park	O_3, $NO/NO_2/NO_x$, THC, SO_2, CO, COH
12.	Sarnia	SO_2
13.	Grace Church	O_3, NO/NO_2, SO_2
14.	Huron View Nurs.	O_3, NO/NO_2
15.	Wyoming	O_3
16.	Thedford	O_3
17.	Parkhill	O_3
18.	London	O_3, $NO/NO_2/NO_x$, SO_2, CO, COH, THC
19.	Huron Park	O_3
21.	Tiverton	O_3, SO_2, TRS
23.	Camlachie	O_3, $NO/NO_2/NO_x$, THC, RHC, SO_2, CO, H_2CO, H_2O_2, hydorcarbons by gas chromatography, ozone precursor monitor
Aircraft		O_3, NO/NO_x, SO_2, HNO_3, particulate SO_4 and NO_3, THC, visibility (nephelometer), hydrocarbons by gas chromatography

---

*See Figure 3 for location

[1] Total hydrocarbons

[2] Reactive hydrocarbons

[3] Coefficient of haze

Table 2

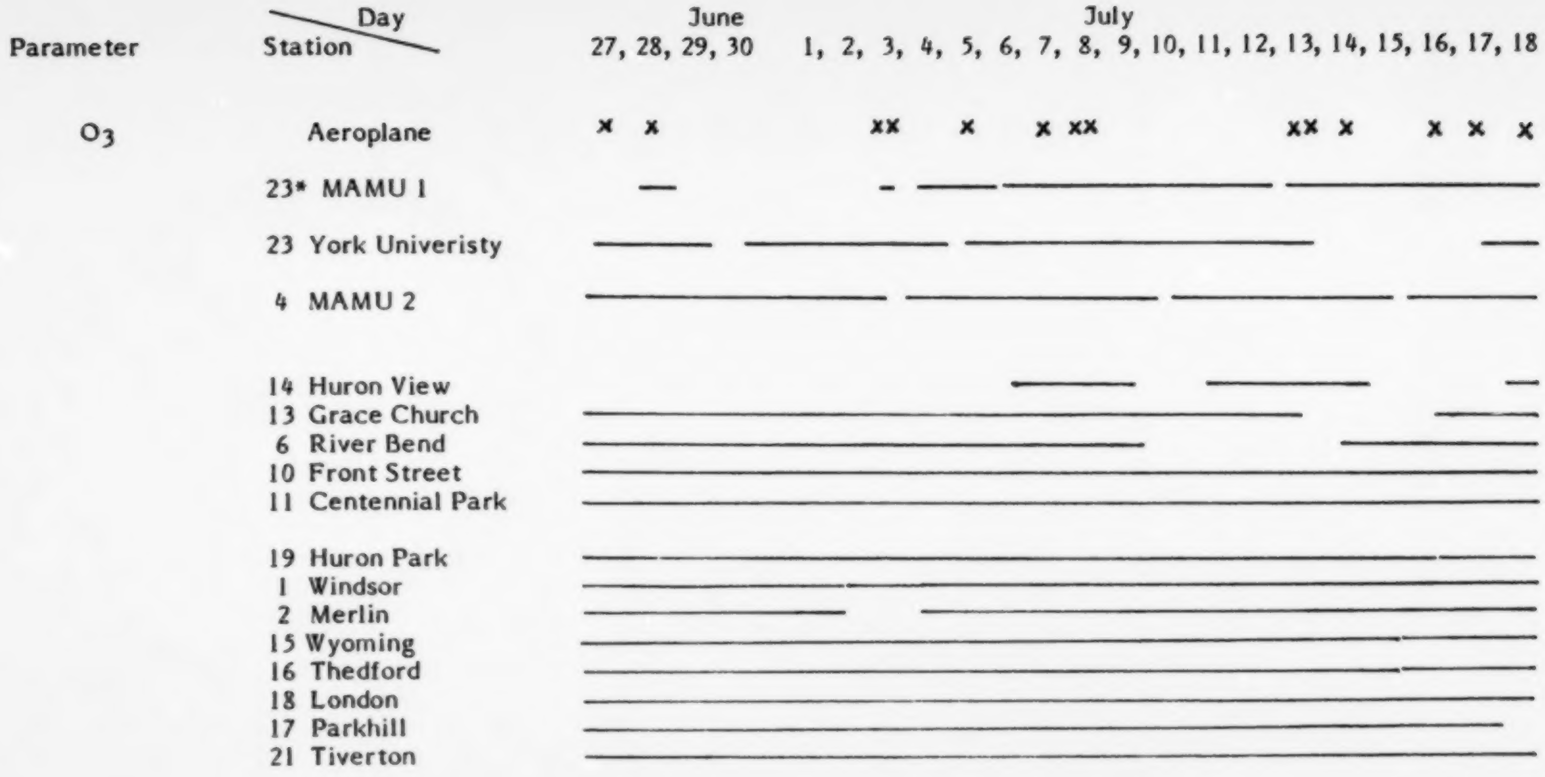
Summary of Meteorological Data Available from Sarnia Area During the Sarnia Oxidants Study

	Location	Instrumentation	Height of Sensor
23*	Camlachie	Minisonde	-
		Wind sp./dir./temp.	10 m
24	Petrolia	Minisode, Acoustic sounder	-
4	Courtright	Wind sp./dir./temp.	10, 30, 91 m
5	Sixth Line	Wind sp./dir.	10 m
6	River Bend	Wind sp./dir.	10 m
7	LaSalle Road	Wind sp./dir.	10 m
9	River Front	Wind sp./dir.	10 m
10	Front Street	Wind sp./dir.	10 m
12	Indian Road S.	Wind sp./dir.	9 m
17	Parkhill	Wind sp./dir.	10 m
20	Grand Bend	Wind sp./dir.	10 m
22	Tiverton	Wind sp./dir./temp.	10, 30, 100 m
2	Merlin	Wind sp./dir.	9 m

*See Figure 3 for locations

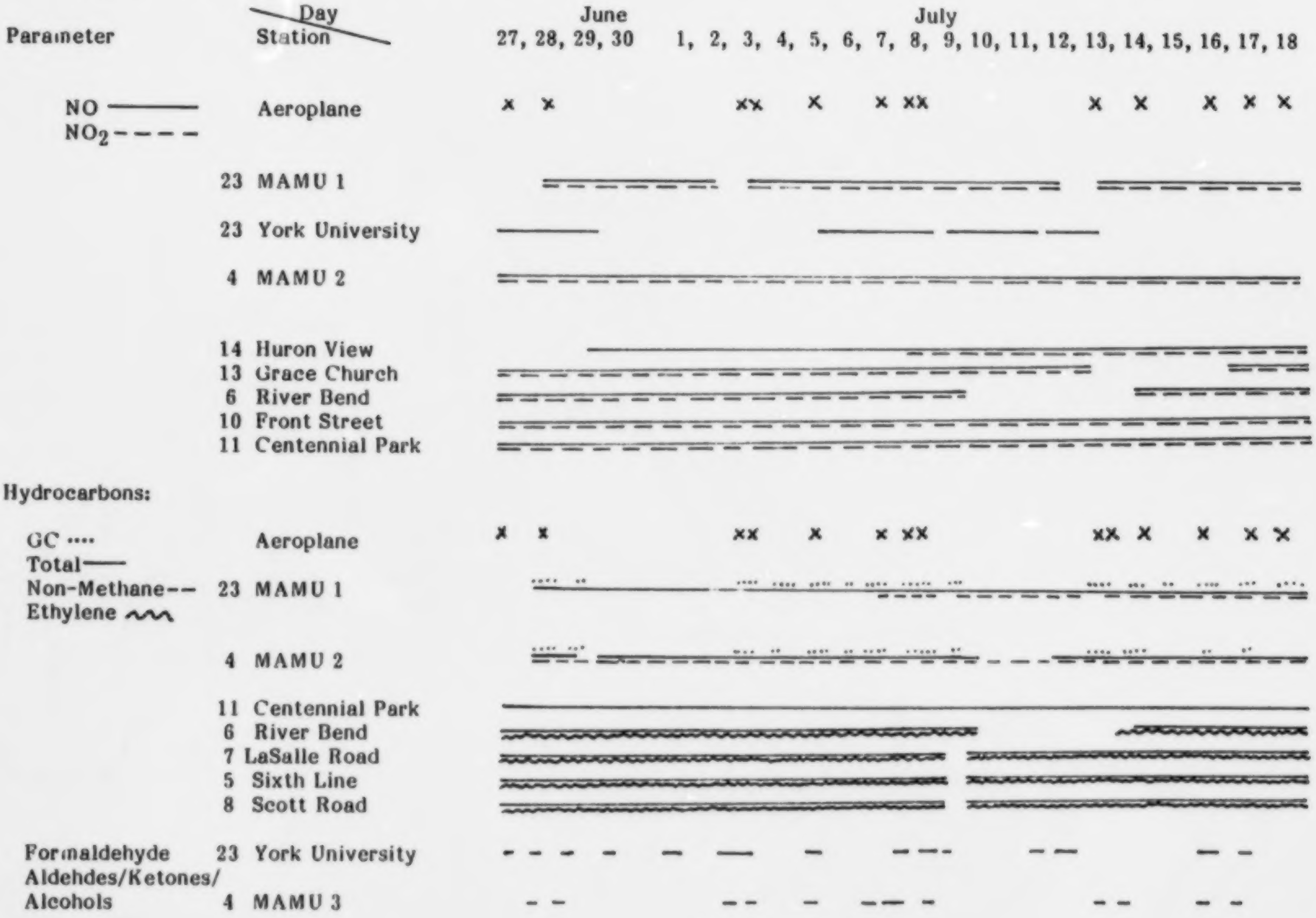
Table 3

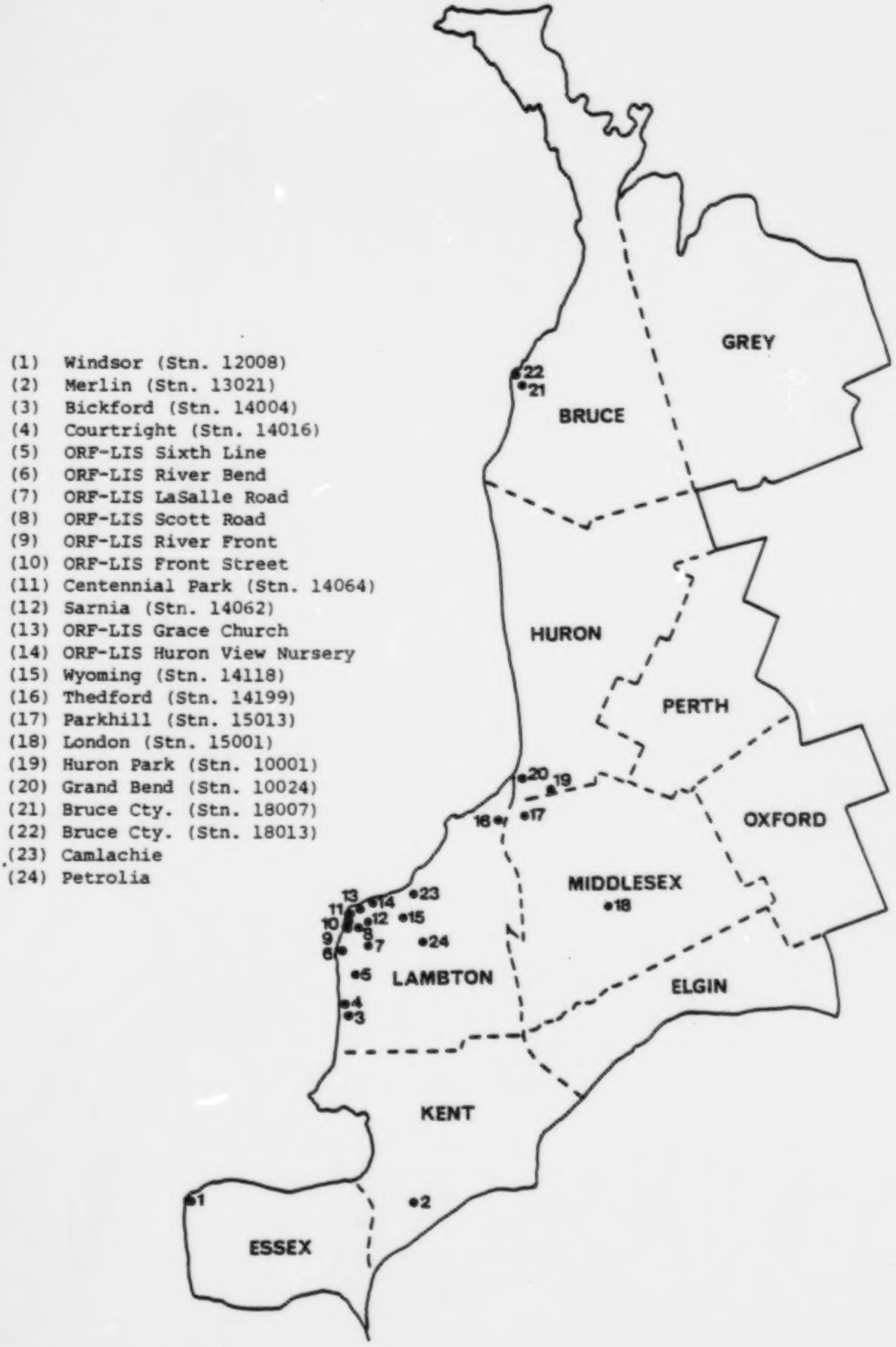
Summary of Available Air Quality Data from Sarnia Oxidants study 1984



*See Figure 3 for locations

Table 3 (Continued)




GREY
BRUCE
HURON
PERTH
OXFORD
MIDDLESEX
LAMBTON
ELGIN
KENT
ESSEX
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(1) Windsor (Stn. 12008)
(2) Merlin (Stn. 13021)
(3) Bickford (Stn. 14004)
(4) Courtright (Stn. 14016)
(5) ORF-LIS Sixth Line
(6) ORF-LIS River Bend
(7) ORF-LIS LaSalle Road
(8) ORF-LIS Scott Road
(9) ORF-LIS River Front
(10) ORF-LIS Front Street
(11) Centennial Park (Stn. 14064)
(12) Sarnia (Stn. 14062)
(13) ORF-LIS Grace Church
(14) ORF-LIS Huron View Nursery
(15) Wyoming (Stn. 14118)
(16) Thedford (Stn. 14199)
(17) Parkhill (Stn. 15013)
(18) London (Stn. 15001)
(19) Huron Park (Stn. 10001)
(20) Grand Bend (Stn. 10024)
(21) Bruce Cty. (Stn. 18007)
(22) Bruce Cty. (Stn. 18013)
(23) Camlachie
(24) Petrolia

Figure 3: Location of Air Quality and Meteorological Monitoring Sites

3. Summary of Results

This chapter consists of a day-by-day discussion (on days when aircraft samples were being collected) of the meteorological conditions and concurrent air quality in the study area. Particular attention is paid to any evidence of an ozone "plume" downwind of the Sarnia industrial area, and the meteorological conditions, and previous air parcel history, which accompany appreciable downind ozone buildups.

Only the salient features of the data are considered: for detailed data listings the reader is referred to MOE reports ARB-019-85-ARSP, ARB-020-85-ARSP, ARB-021-85-ARSP, ARB-022-85-ARSP, ARB-023-85-AQM and ARB-024-85-ARSP, as well as Hastie and Schiff (1985). Aerial observations of ozone on each day are discussed, including both the aircraft and ground-level measurements. Note that there is a mis-match of the aircraft and the ground-based measurement time frames - the former represent instantaneous values, while the latter are expressed as hourly averages. A series of maps of hourly ozone ground-level observations were plotted during the period when airborne measurments were taken on each day. During each hour, the location of the particular aircraft traverse flown during that hour, as well as the ozone observations made on the aircraft (including the average for the traverse, and maximum and minimum values in ppb) are also shown. No ozone data are shown for urban monitoring sites, as there was frequent evidence of local interferences at these sites, due to scavenging of ozone by nitric oxide emissions. These maps also include the wind speed and direction at the approximate aircraft samping height, as determined from minisonde measurement made at the Petrolia site. Figure 4 contains an explanation of the information on the areal ozone plots to be discussed below.

As was pointed out in Chapter 2, a decision was made to maximize the area covered by the aircraft, at the expense of vertical resolution, by carrying out most flights at a constant level, at about one-third to one-half way to the top of the mixing layer. The generally good agreement between aircraft and ground-level observations, as well as the absence of marked vertical structure on most occasions when spirals were flown, indicates that this was an acceptable procedure, due no doubt largely to the fact that most of the aircraft sampling took place between 1000 and 1500 hours, when atmospheric turbulence helped to create a fairly uniform concentration distribution within the mixing layer. However, there were some notable exceptions, especially in the morning flights when the atmosphere was still relatively stable and mixing was inhibited.

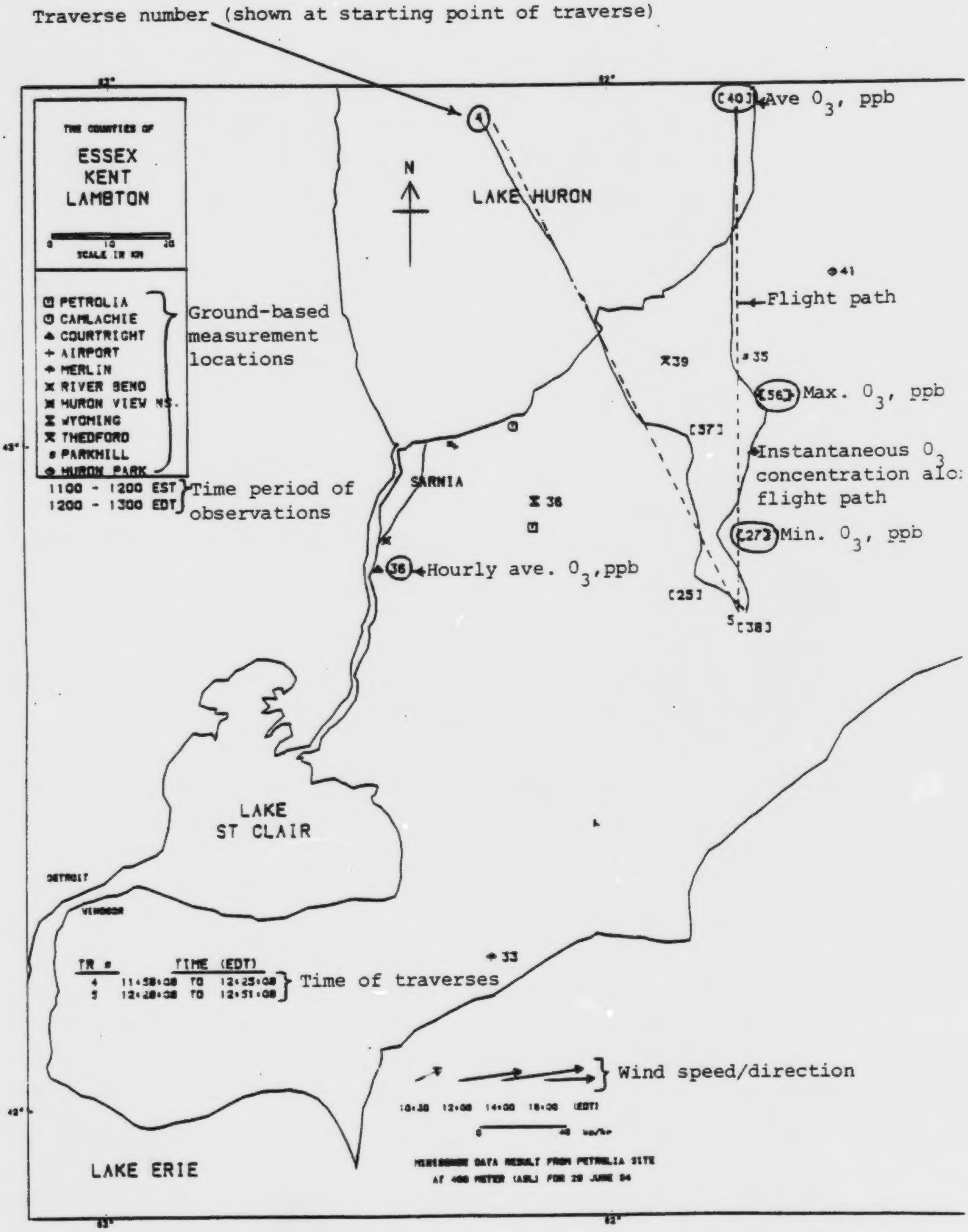

Traverse number (shown at starting point of traverse)
THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
Ground-based measurement locations
1100 - 1200 EST
1200 - 1300 EDT
Time period of observations
N
LAKE HURON
4
[40]
Ave O_3, ppb
41
Flight path
35
39
[56]
Max. O_3, ppb
[37]
Instantaneous O_3 concentration alo
flight path
SARNIA
38
[27]
Min. O_3, ppb
36
Hourly ave. O_3,ppb
[25]
5
[38]
LAKE
ST CLAIR
DETROIT
WINDSOR
33
TR #
TIME (EDT)
4 11:58:08 TO 12:25:08
5 12:28:08 TO 12:51:08
Time of traverses
Wind speed/direction
10:30
12:00
14:00
16:00
(EDT)
0
40 km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 400 METER (ASL) FOR 28 JUNE 84
LAKE ERIE
43°
42°
83°
82°

Figure 4: Sample Map of Ozone Observations in the Sarnia Area

3.1 June 27

A well-developed low pressure system was centered over Sault Ste. Marie on the morning of June 27, and moved very slowly northward throughout the day. The cold front associated with this low passed throught the Sarnia region during the afternoon and as a result, the southerly flow in the morning shifted to westerly by afternoon, at the time of the aircraft flights. For the period 1300-1700 EDT, winds were westerlies, generally in the 25-35 km h^{-1} range, occasionally gusting to 40-50 km h^{-1}. Cloudy skies prevailed, with surface temperatures near the mid-twenties (centigrade), and a relative humidity of about 60%. The minisonde data at Camlachie and Petrolia during the above period suggests a mixed layer height in excess of 1500 m.

Backward trajectories (48 hours) of air parcels over the Sarnia area during the study period indicate an air path from Nebraska east-north-eastwards to Sarnia. Forward trajectories from Sarnia for the same period show a general east-north-eastward movement.

Figure 5 shows the hourly average ozone concentrations throughout the day at a number of monitoring locations in the study area. Levels are low-generally less than 50 ppb - with little diurnal variation. The aircraft data collected upwind of Sarnia also indicate a relatively clean air mass entering the study area, with ozone concentrations in the 36-43 ppb range (gradually increasing from north to south), good atmospheric visibility (b_{scat} values, as measured by the nephelometer, were about 1×10^{-4} m^{-1}), NO_x levels less than 10ppb, and sulfates and nitrates at 12 and 1.3 ug m^{-3} respectively - see Figure 7. Figures 6(a) and (b) show the concurrent aircraft and ground-level ozone observations on June 27 during the period of 1500 - 1700 EDT. The aircraft samples were taken at about 300 m above ground level. The aircraft ozone data show few features, other than a local dip in ozone levels during traverses 3, 4 and 5 (Figure (6b)), which the concurrent NO_x measurements indicate to be due to scavenging by a plume with elevated NO_x concentrations, possibly from the generating stations near Courtright; and a sharp peak during traverse 3, which is probably due to a power fluctuation (as can be seen from Figure 7, several other instruments on board the aircraft also showed a temporary irregularity at that time). Otherwise the upwind and downwind aircraft traverses are similar, with no indication of an ozone buildup attributable to Sarnia, at least, not within the first hour or two of air parcel travel time (after crossing Sarnia) examined during this flight. Except as noted above, the levels of the other parameters measured aboard the aircraft on this flight also showed little variation. The ground-level monitors at Merlin and Tiverton, which were well clear of any Sarnia emissions, did suggest lower ozone levels (by about 10 ppb, hourly average) than monitors downwind of Sarnia (see Figures 5 and 6(a) and (b)), but this apparent ozone buildup is not thought to be due to Sarnia, because the upwind aircraft traverse (Figure 6(a)) shows that this buildup is probably due to other, upwind sources.

The hydrocarbon samples collected at Courtright and Camlachie during the afternoon showed very low levels (about 15 micrograms per cubic meter, or less, of propane plus higher molecular weight compounds), consisting largely of alkanes. The two aircraft samples, collected during traverses 1 and 2, and 3 and 4, had considerably higher concentration (120 and 134 ug m^{-3} respectively), with about 80% of the total mass being attributable to aromatics. Since the aircraft samples were exposed, at least during part of the time, directly downwind of Sarnia sources, it is difficult to determine whether the elevated concentrations are due to an elevated emissions source at Sarnia, or to sample contamination. Unfortunately, the photoionization hydrocarbon detector on board the aircraft, which may have assisted in the interpretation of these results, was not operational on this day.

Much of the information on other chemical parameters of interest, as measured at Courtright and Camlachie, is unavailable for the afternoon of June 27, with the exception of some data collected by the York University group (at Camlachie). Very low levels of NO (0.3 ppb or less) were observed, from about noon onwards, with the high-sensitivity NO analyser. In the late afternoon and evening, formaldehyde and hydrogen peroxide were monitored with the tunable diode laser spectrometer. Formaldehyde levels were constant at about 1 ppb, while hydrogen peroxide varied between about 0.2 and 1.3 ppb.

In summary, on June 27 - an overcast day with brisk westerly winds - ozone levels, as well as those of other pollutants, were low throughout the study area. There was no evidence of any ozone buildup downwind of Sarnia, although an upwind ozone plume from an unknown source area was suggested by the aircraft data.

JUNE 27

TIME VS. OZONE CONCENTRATION

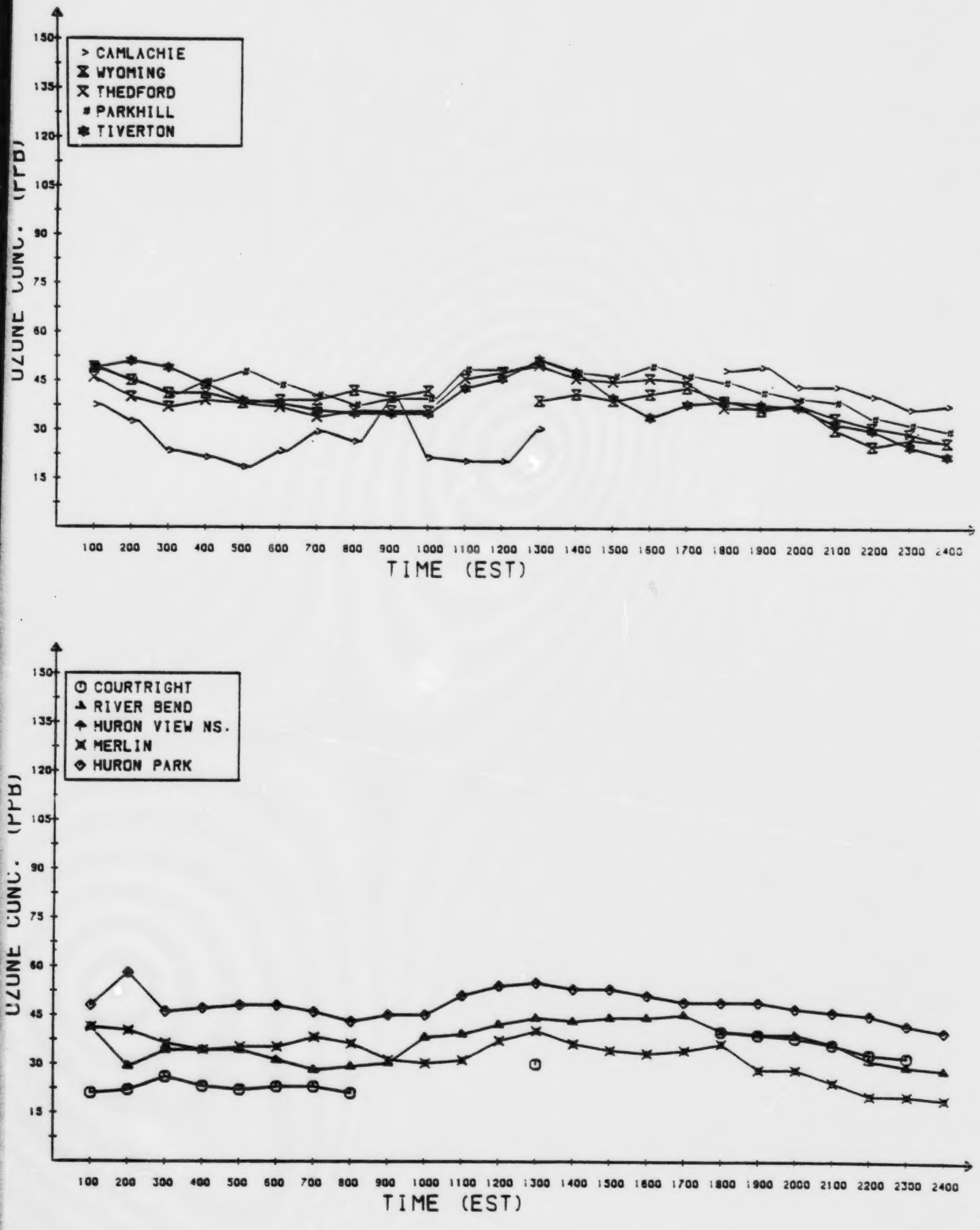


Figure 5: Diurnal Variation of Ozone Concentrations in the Sarnia Area, June 27

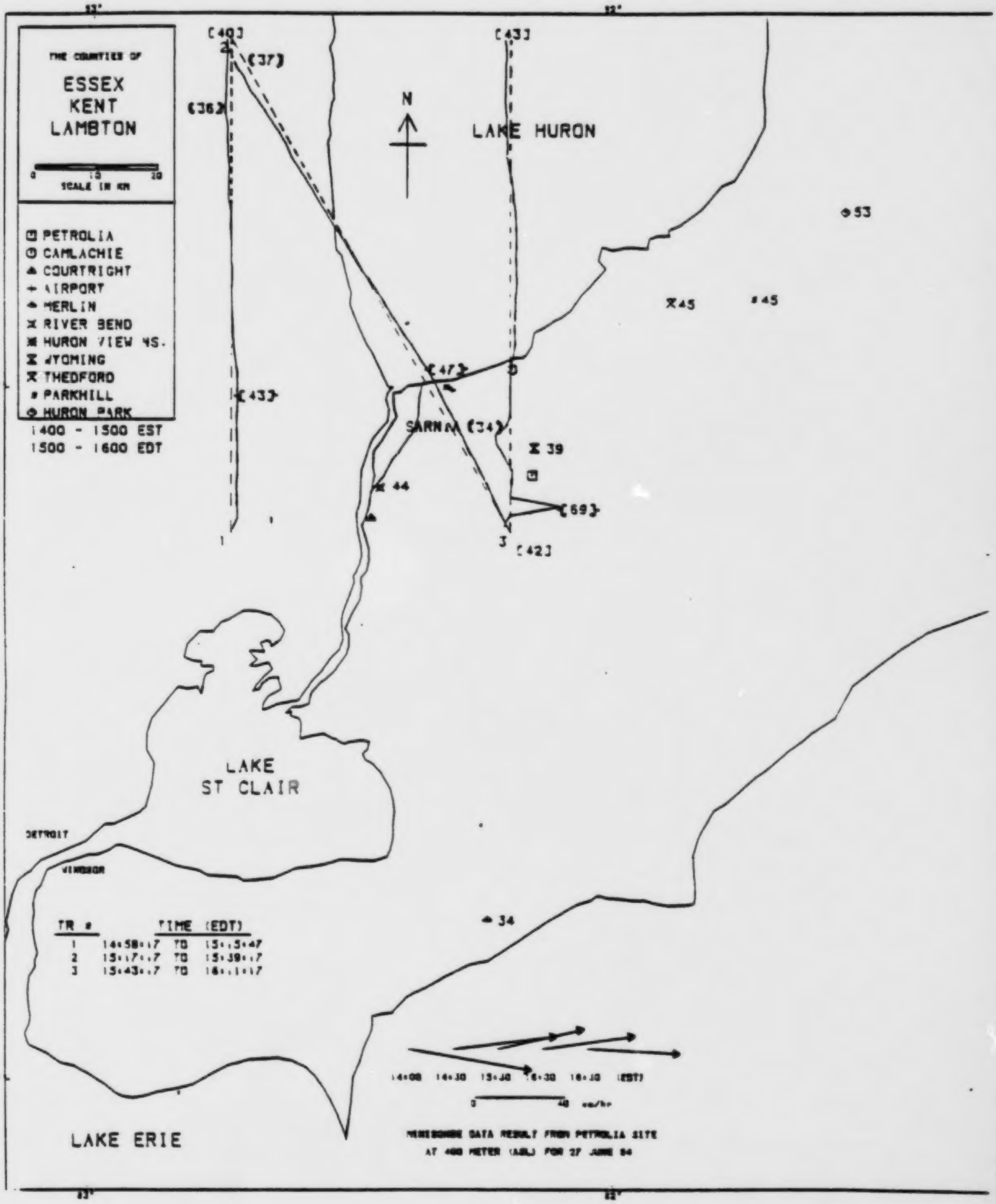

THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW HS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
1400 - 1500 EST
1500 - 1600 EDT
N
LAKE HURON
[40]
[37]
[36]
[43]
2
[43]
[47]
SARNIA
[34]
39
44
[69]
1
3
[42]
53
45
45
LAKE
ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
1 14:58:17 TO 15:15:47
2 15:17:17 TO 15:39:17
3 15:43:17 TO 16:11:17
34
14:00
14:30
15:30
15:30
16:30
(EST)
0
40
km/hr
DATA RESULT FROM PETROLIA SITE
AT 400 METER (AGL) FOR 27 JUNE 84
LAKE ERIE
83°
82°
43°
42°

Figure 6(a): Ozone Observations in the Sarnia Area on June 27, 15-16 EDT

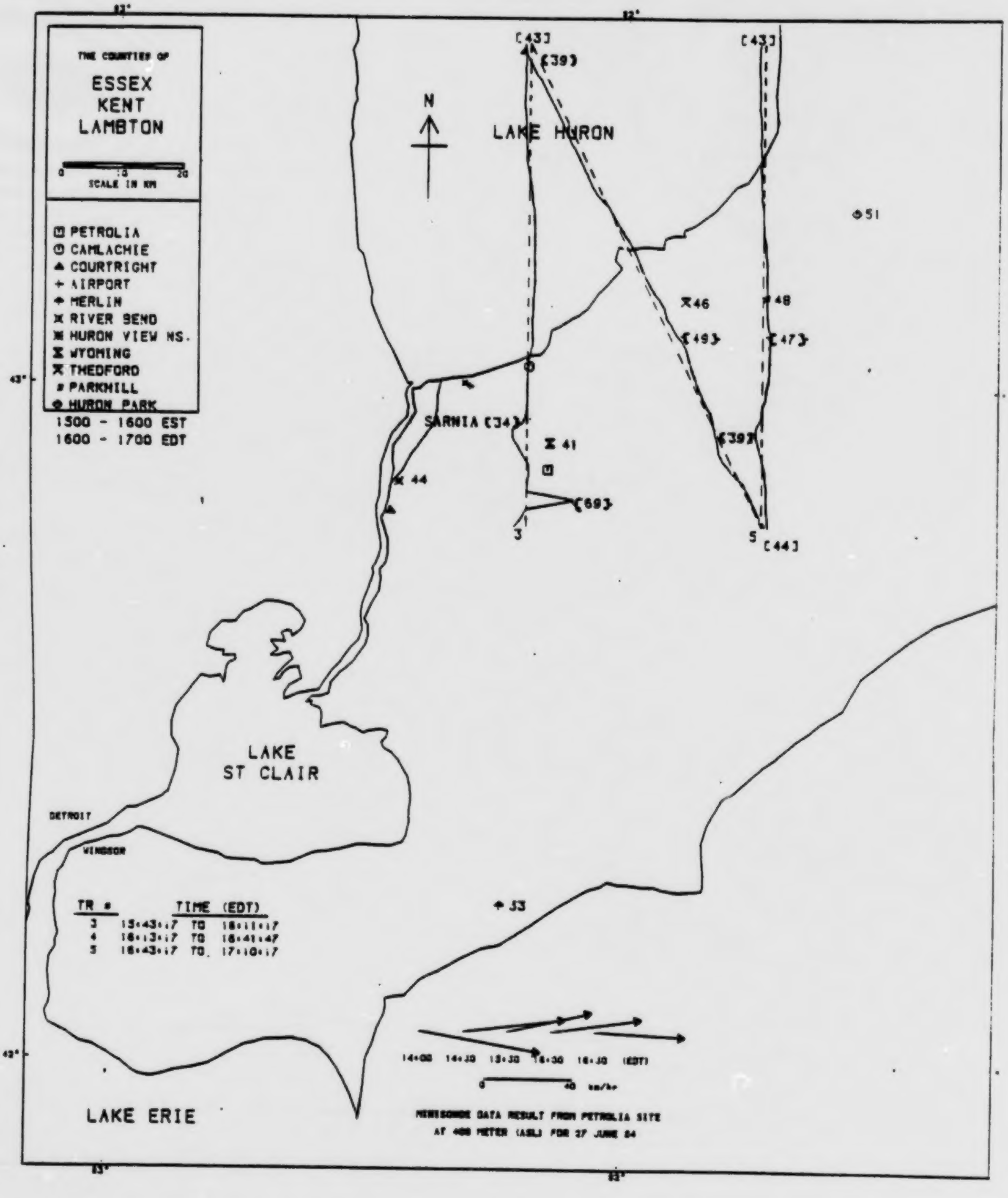

83°
82°
THE COUNTIES OF
ESSEX
KENT
LAMBTON
0 10 20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
1500 - 1600 EST
1600 - 1700 EDT
N
LAKE HURON
[43]
[39]
[43]
51
46
48
[49]
[47]
43°
SARNIA [34]
41
44
[39]
[69]
3
5
[44]
LAKE ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
3 15:43:17 TO 16:11:17
4 16:13:17 TO 16:41:47
5 16:43:17 TO 17:10:17
53
14:00 14:30 15:30 15:30 16:30 (EDT)
0 40 km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 400 METER (ASL) FOR 27 JUNE 84
42°
LAKE ERIE
83°
82°

Figure 6(b): Ozone Observations in the Sarnia Area on June 27, 16-17 EDT

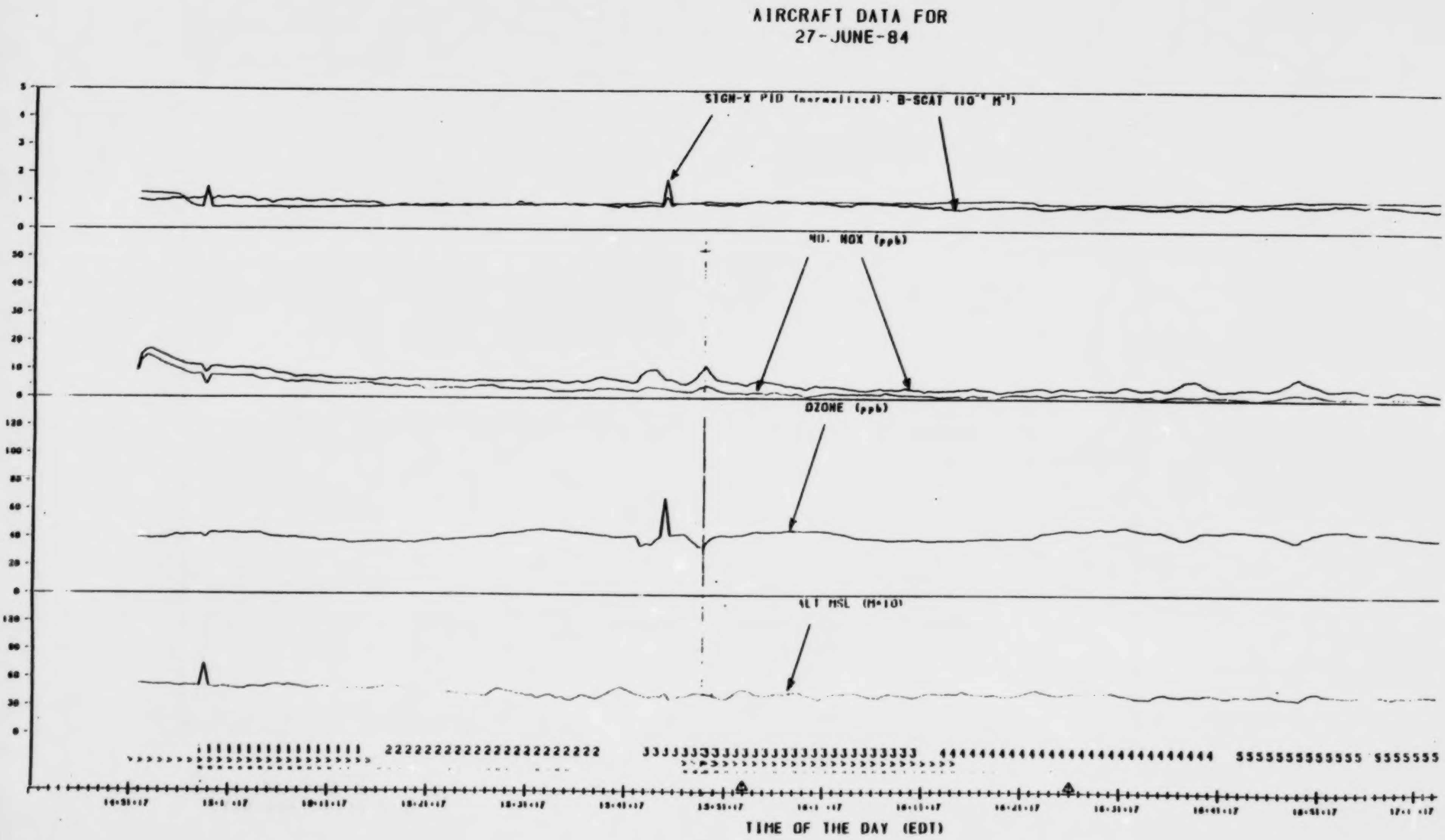


Figure 7: Aircraft Observations on June 27

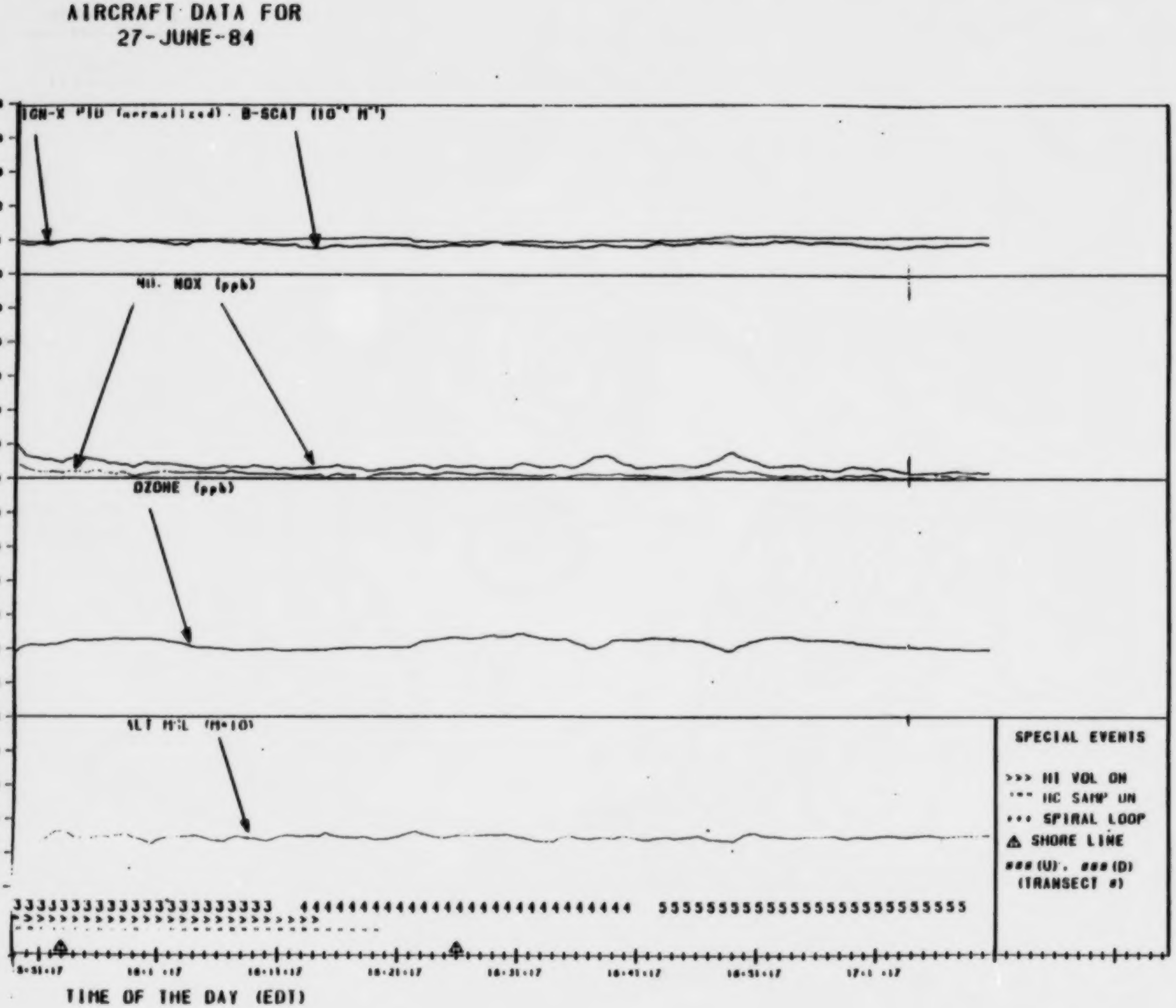


Figure 7: Aircraft Observations on June 27 (continued)

3.2. June 28

The previously-mentioned low pressure system, now located south of James Bay, resulted in a cyclonic westerly flow over the Sarnia region. For the sampling period of interest (0900 - 1300 EDT), westerly winds prevailed, with wind speeds typically in the 5 to 20 km h^{-1} range. Skies were mainly sunny, with surface temperatures in the low to mid-twenties, and a maximum observed hourly average total solar radiation (in the 0.3 to 3 micron range) of 112 milliwatts per cm^2. The relative humidity was in the range of 40-50%. The minisonde data at Camlachie and Petrolia during the period 0900 - 1300 EDT suggest an initial mixed layer height of approximately 600 m, which increased to about 2000 m by early afternoon.

Backward trajectories (48-hour) of air parcels during this period indicate a path from the western edge of Lake Superior southeastward to Sarnia, with no significant ozone precursor sources along the way. Probably as a result of this fact, ozone levels in the study area were generally low, with hourly average values of about 40 ppb in the early afternoon. Figure 8 shows the variation in ozone concentrations throughout the day at a number of monitoring stations in the area.

The concurrent aircraft and ground-level ozone observations on June 28 (during the period 1000 - 1400 EDT) are shown in Figures 9(a)-(d). The aircraft sampled at about 200 m above ground level. The upwind traverse (see Figures 9(a) and 10) showed fairly uniform ozone concentrations of about 30 ppb, and NO_x concentrations near the instrument detection limit (about 5 ppb). Light - scattering particulates, as measured by the nephelometer, were relatively low (b_{scat} of about 1.1 - 1.3 x 10^{-4} m^{-1}). The upwind sulfate and sulfur dioxide levels determined by the high-volume filter pack on the aircraft were 12 and 25 ug m^{-3} respectively, which seems rather high for the otherwise apparently clean background air, and may be due to sample contamination.

The traverses conducted about 10-15 km downwind of Sarnia showed a local sharp decrease in the ozone, with concurrent increases in NO_x and light-scattering particulate levels, just south of the Sarnia industrial area (Figures 9 (b) and 10). This is due to scavenging of ozone by NO from Ontario Hydro's Lambton generating station's emissions at Courtright, and possibly emissions from the nearby Detroit Edison St. Clair and Belle River plants on the U.S.A. side of the border. Directly downwind of the industrial area, there was no evidence of any ozone buildup in these traverses, which represent a Sarnia plume travel time (based on the minisonde wind measurements at about 200 metres) of less than one hour.

However, about 40-60 km from Sarnia, or after 2-3 hours of air parcel travel time (traverses 4 and 5 on Figure 9(c)), an elevation of ozone (about 15-20 ppb maximum above the regional average values) was evident in the measurements, approximately downwind of the Sarnia industrial area. The NO_2 (but not NO) levels in the 10-15 km-wide ozone plume were found to increase somewhat, and there was also an increase in light-scattering particulates (to approximately two times the values measured upwind) - see Figure 10. Just to the south of the ozone plume, a decrease in ozone was observed, with concurrent sharp increases in NO_x and b_{scat}, which is again attributable to the above - mentioned generating stations.

Similar features were noted in the final two traverses (6 and 7, Figure 9(d)), at more than 60 km from Sarnia, and there was also a suggestion of an ozone plume from the Windsor-Detroit area, just over the north shore of Lake Erie. Although a comparison of Figures 9(c) and 9(d) strongly suggests that the same plumes are being observed in both figures, it is not clear why there is such a large shift southward in the more distant observations (Figure 9(d)), since there is no evidence of any significant wind change during the period when the traverses were being carried out. As with traverses 4 and 5, so also with 6 and 7, the areas having elevated ozone levels also showed appreciable increases in the light-scattering particulates, and less pronounced, though significant, buildups of NO_2.

Thus the aircraft data on June 28th, a clear day with brisk winds, generally clean background air and low maximum ozone levels, show strong evidence of an ozone plume downwind of the Sarnia industrial area, with values elevated by more than 30% above the regional levels. A number of additional observations made on June 28 may be of significance:

The ozone buildup was apparently only observable after more than about one hour of plume travel time from Sarnia. It was not evident in the close-in traverses (2 and 3), nor in the downwind ground-level station at Wyoming, which was recording regionally representative levels even while the aircraft was measuring elevated values at a nearby downwind location (traverses 4 and 5).

Aircraft filter pack samples showed elevated sulfate and nitrate levels downwind of Sarnia, as well as high sulfur dioxide on some traverses. For example, downwind sulfates ranged between 20-32 ug m^{-3} (c.f. 12 ug m^{-3} upwind); nitrates were in the 2-9.7 ug m^{-3} range (c.f. 1.6 ug m^{-3} upwind); sulfur dioxide varied between 22 and 43 ug m^{-3} (25 ug m^{-3} upwind). However, since all the downwind traverses also crossed the plumes from the above - mentioned generating stations, it is not clear what portion of these values can be attributed to emissions from the Sarnia industrial area, and how much is due to the power plants. Because of similar interpretation problems in other flights, details of the downwind filter pack measurements will not be discussed in subsequent sections.

During the morning, measurements within Sarnia for NO_x and hydrocarbons, at a number of stations where these parameters are routinely monitored, showed values generally comparable to the monthly mean values, i.e. there was no evidence for any buildup of ozone precursors. During the sampling period itself, hydrocarbon samples collected downwind of Sarnia, both at Camlachie and aboard the aircraft, showed levels at or below the averages observed during the overall survey for total hydrocarbons, alkanes and aromatics, and non-detectable alkene levels. NO_x levels were generally at or near detection limits (i.e. less than 5 ppb), except when the aircraft crossed generating station plumes. At Camlachie, where high-sensitivity NO measurements were being made by York University, NO levels were below 3 ppb throughout the day.

A few additional measurements of some chemical species, of interest to photochemical smog formation, are available from the Courtright and Camlachie locations. A number of aldehydes and ketones (not including formaldehyde) were surveyed around noon by the TAGA unit at Courtright, and except for traces of propanal and acetone, were found to be below detection limits (0.1-0.3 ppb). During the late morning and early afternoon, formaldehyde levels of about 2 ppm (hourly average) were noted at Camlachie. Hydrogen peroxide levels of 1-3 ppb were also observed here in the late afternoon.

JUNE 28

TIME VS. OZONE CONCENTRATION

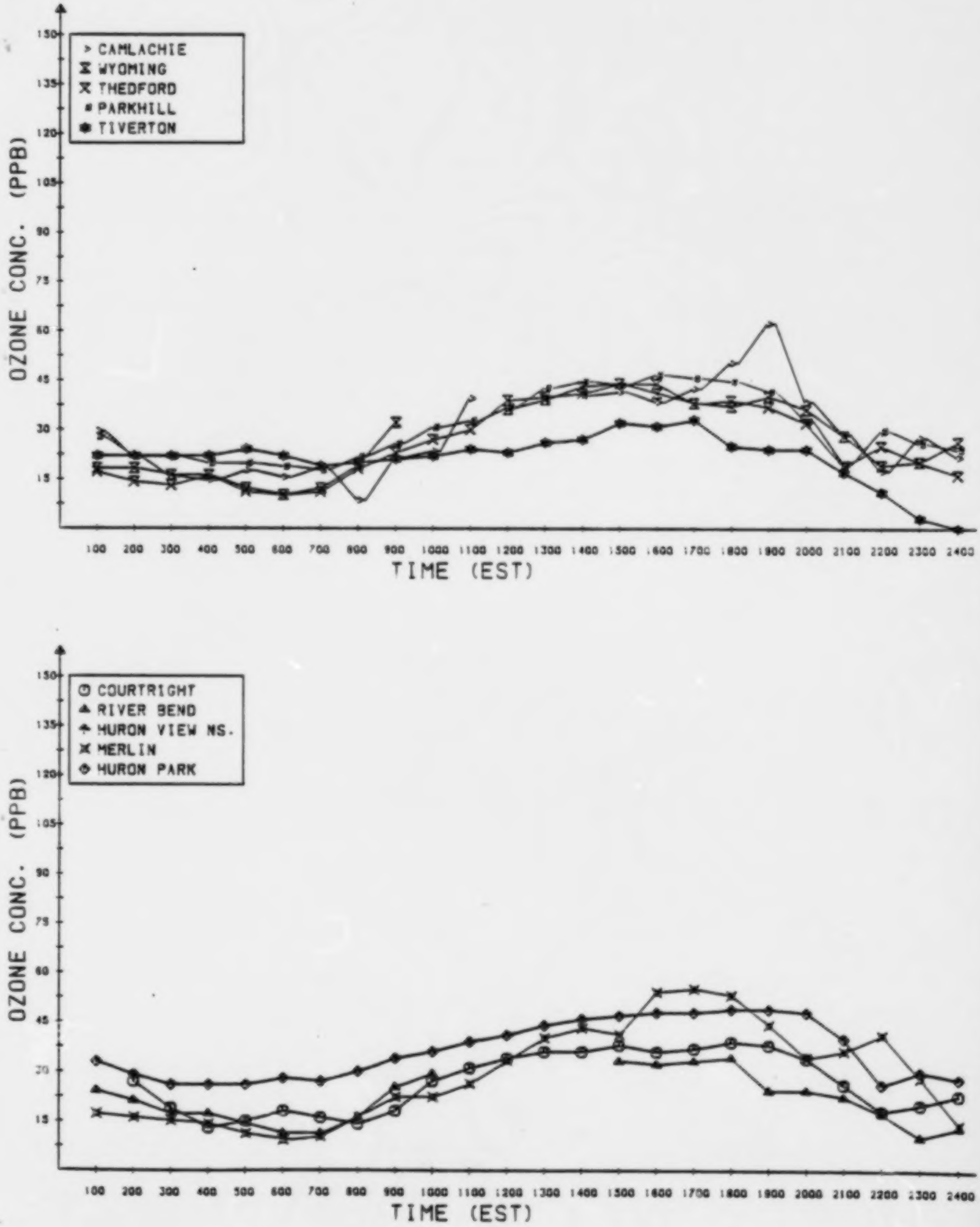


Figure 8: Diurnal Variation of Ozone Concentrations in the Sarnia Area, June 28

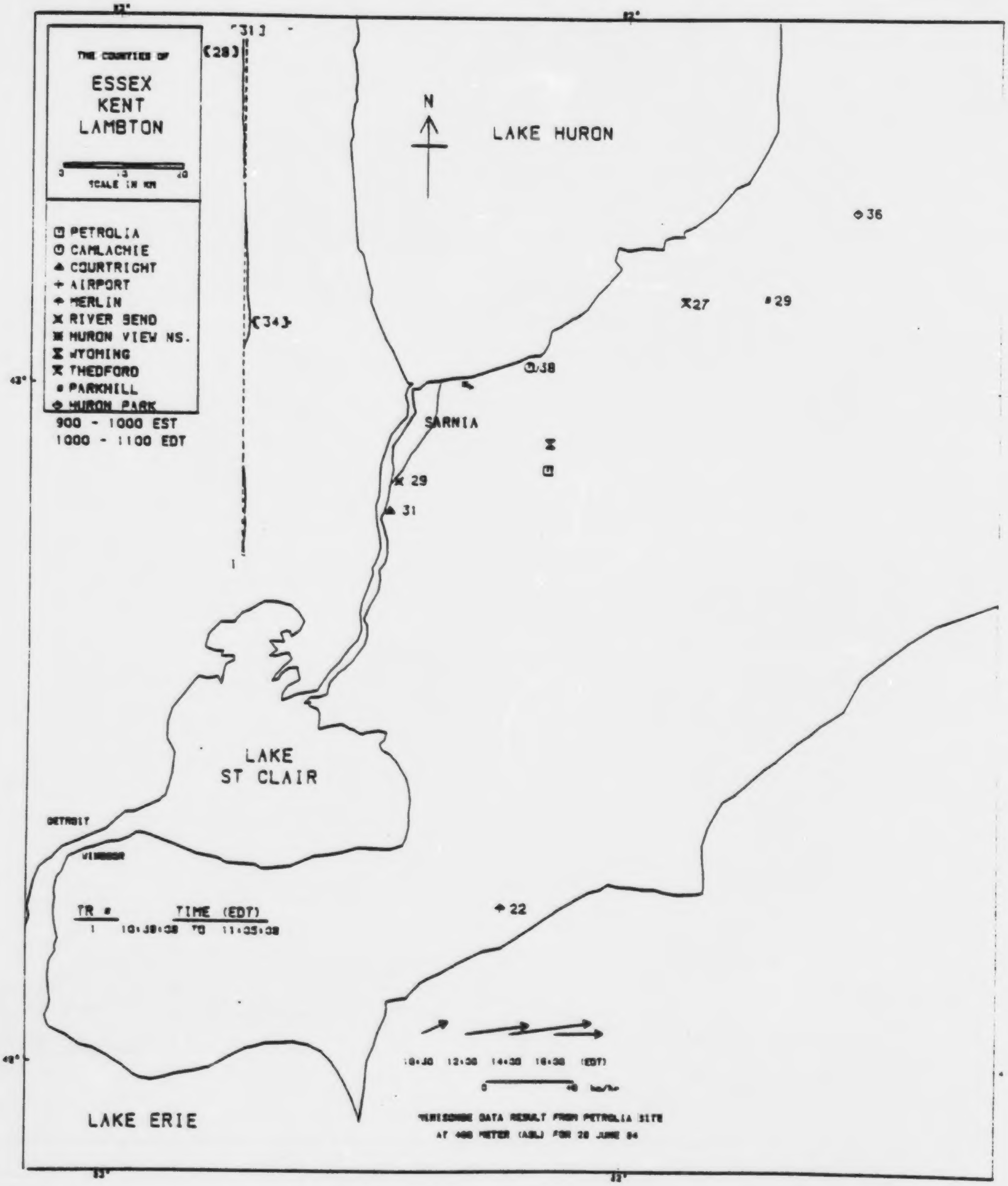

THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
40
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
900 - 1000 EST
1000 - 1100 EDT
[31]
(28)
(34)
N
LAKE HURON
36
27
29
38
SARNIA
29
31
LAKE
ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
1
10:38:38 TO 11:35:38
22
10:30
12:30
14:30
16:30
(EDT)
0
LAKE ERIE
AT 400 METER (ASL) FOR 28 JUNE 84

Figure 9(a): Ozone Observations in the Sarnia Area on June 28, 10-11 EDT

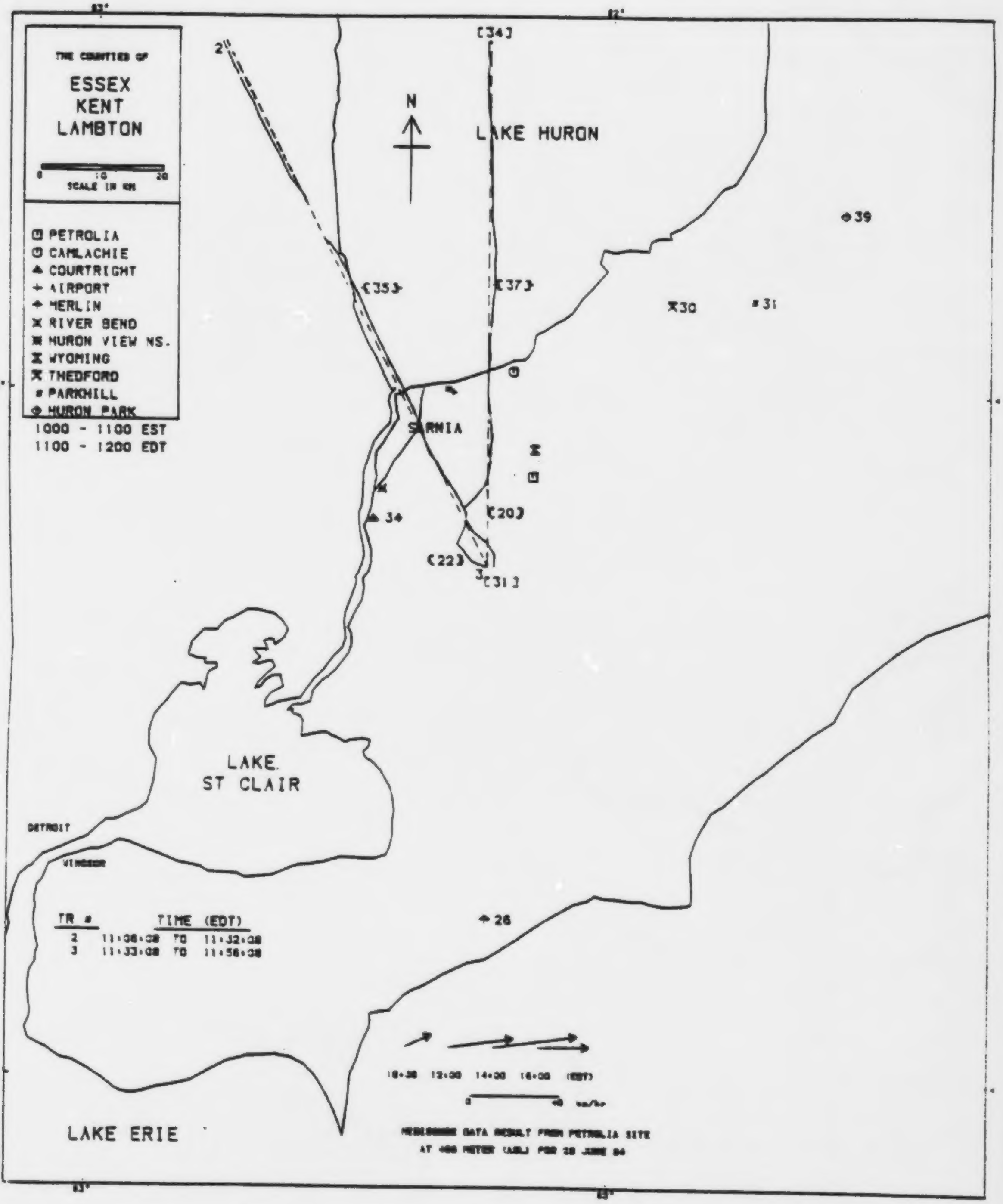

83°
82°
THE COUNTIES OF
ESSEX
KENT
LAMBTON
0 10 20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
1000 - 1100 EST
1100 - 1200 EDT
43°
42°
2
[34]
N
LAKE HURON
39
[35]
[37]
30
31
SARNIA
34
[20]
[22]
3
[31]
LAKE ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
2 11:06:38 TO 11:32:38
3 11:33:08 TO 11:56:38
26
10:30 12:00 14:00 16:00 (EDT)
0 40 km/hr
MESOSONDE DATA RESULT FROM PETROLIA SITE
AT 400 METER (AGL) FOR 28 JUNE 84
LAKE ERIE

Figure 9(b): Ozone Observations in the Sarnia Area on June 28, 11-12 EDT

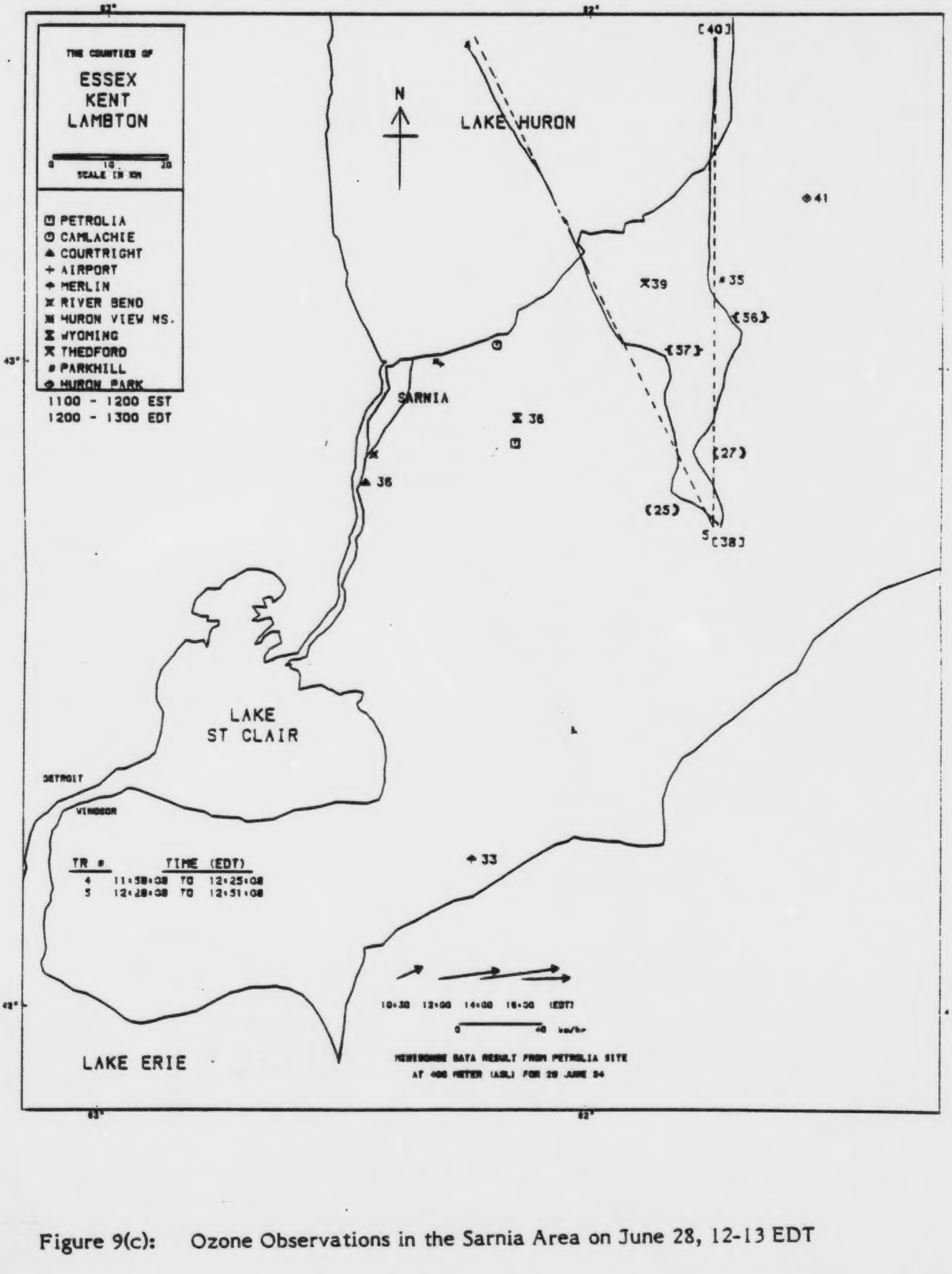

83°
82°
43°
42°
THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW HS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
1100 - 1200 EST
1200 - 1300 EDT
N
LAKE HURON
[40]
41
39
35
{56}
{37}
SARNIA
36
36
[27]
(25)
5
[38]
LAKE
ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
4 11:58:08 TO 12:25:08
5 12:28:08 TO 12:51:08
33
10:30
12:00
14:00
16:30
(EDT)
0
40
km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 400 METER (ASL) FOR 28 JUNE 84
LAKE ERIE

Figure 9(c): Ozone Observations in the Sarnia Area on June 28, 12-13 EDT

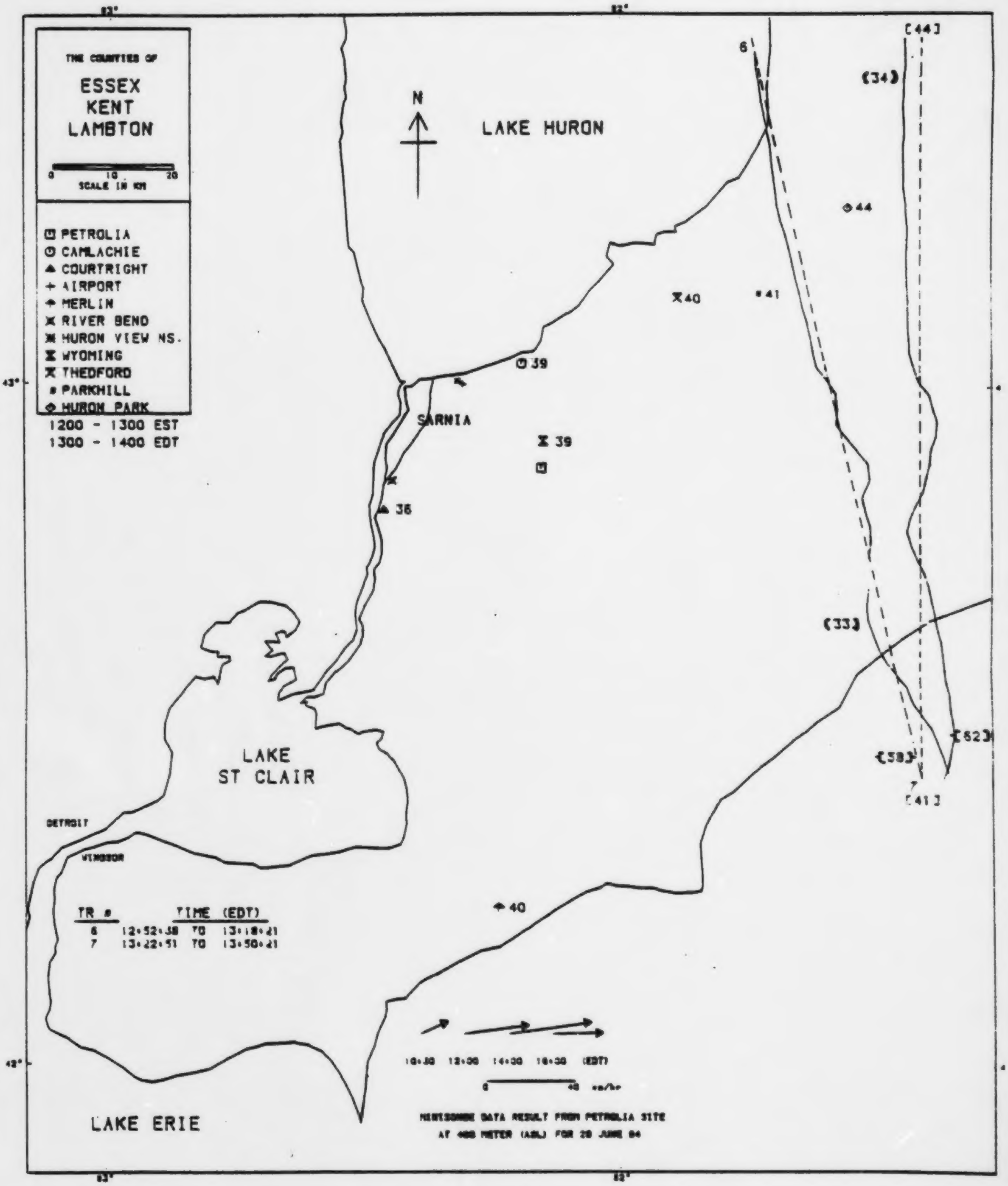

83°
82°
43°
42°
THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
1200 - 1300 EST
1300 - 1400 EDT
N
LAKE HURON
SARNIA
39
39
36
40
41
44
6
7
[44]
(34)
(33)
[62]
(58)
[41]
LAKE
ST CLAIR
DETROIT
WINDSOR
40
TR #
TIME (EDT)
6 12:52:38 TO 13:18:21
7 13:22:51 TO 13:50:21
10:30 12:00 14:30 16:30 (EDT)
0
40 km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 400 METER (ASL) FOR 28 JUNE 84
LAKE ERIE

Figure 9(d): Ozone Observations in the Sarnia Area on June 28, 13-14 EDT

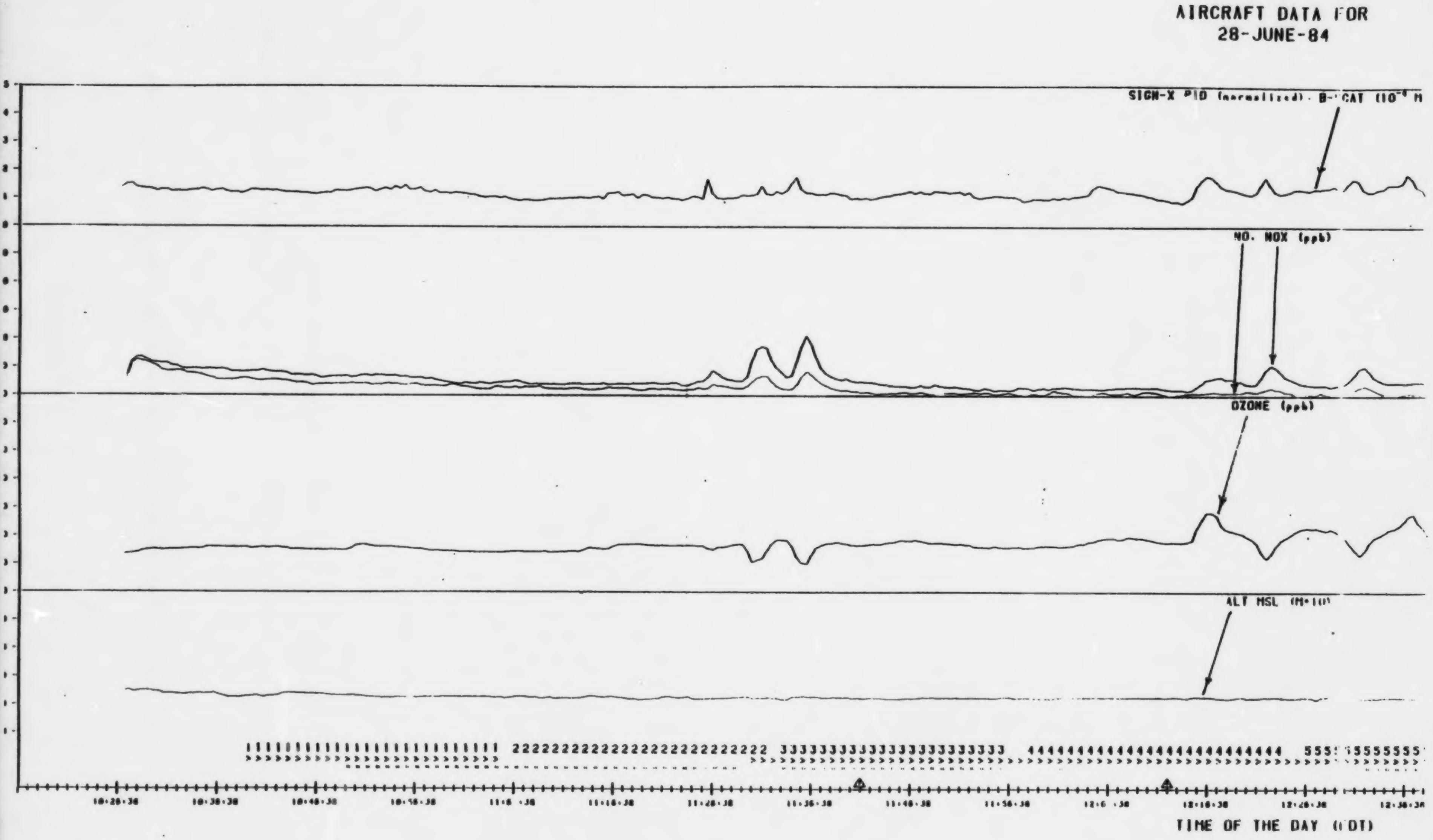


Figure 10: Aircraft Observations on June 28

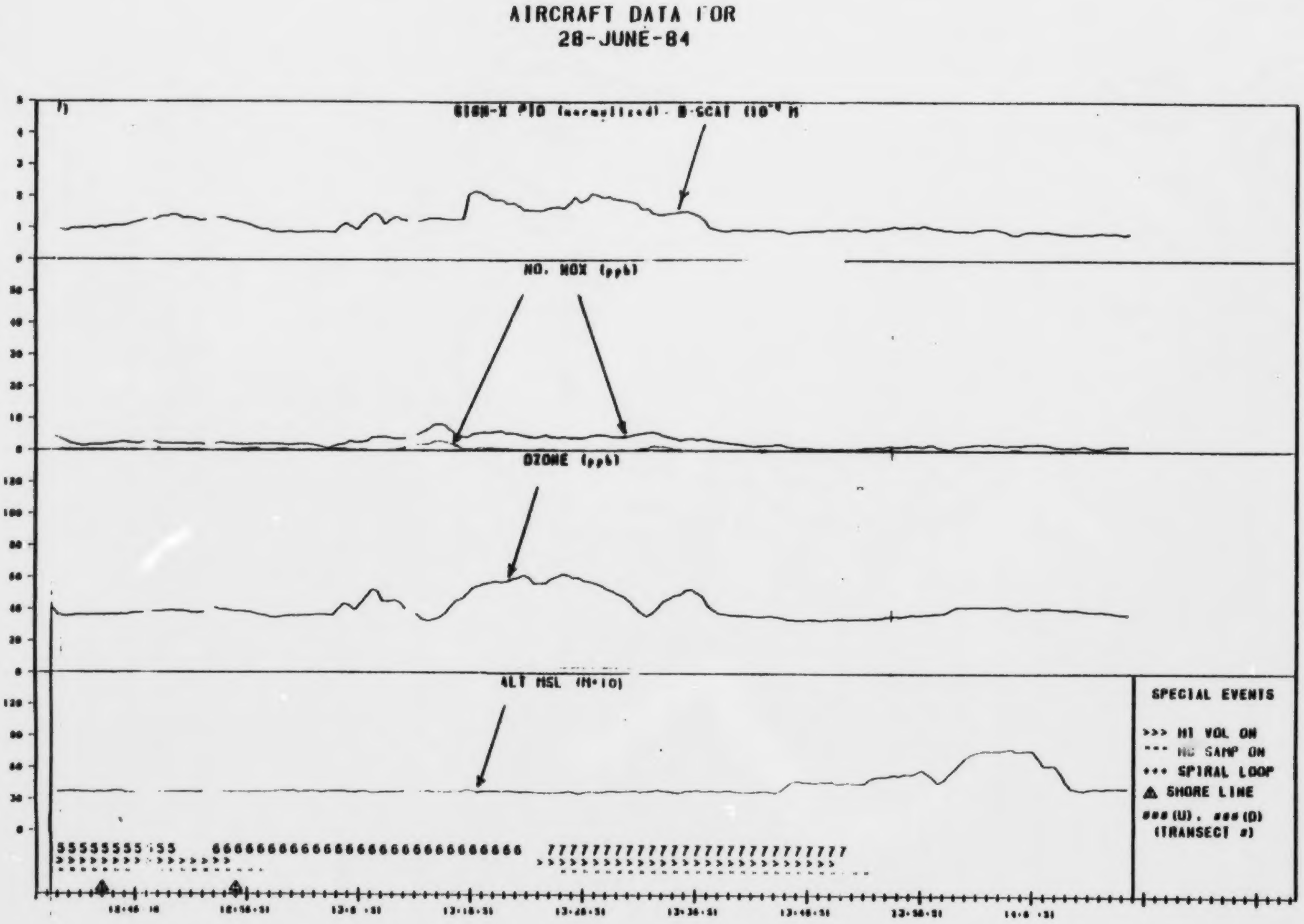


Figure 10: Aircraft Observations on June 28 (continued)

3.3 July 3

On July 3, a "back-of-high" situation developed, the region being dominated by southwesterly flow on the return side of a high pressure cell centered off the Carolinas. Accordingly for the period of interest, 1000-1800 EDT, winds were generally from the southwest, at 10 to 20 km h^{-1}, although occasionally southerly or westerly winds occurred. Sky cover ranged from scattered clouds in the morning to broken clouds (i.e. greater than 5/10 cloud cover) in the afternoon, with surface temperatures in the mid-to upper twenties. The relative humidity during the late morning and throughout the afternoon was observed to be about 50% at Courtright and Camlachie. The maximum hourly average total solar radiation was 101 milliwatts per cm^2. The minisonde data at Camlachie and Petrolia during the above period suggest an initial mixed layer height of approximately 1000 m, increasing to about 2000 m by early afternoon. By 1600 EDT, the mixing height collapsed and the air near the ground became stable.

Forward air trajectories from Sarnia during the study period showed a northeasterly movement. Backward trajectories (48 hours) also indicate a northeasterly path from Indiana and Illinois to Sarnia. Because of these large upwind source areas of ozone precursors, ozone levels over the study area were high, especially during the afternoon (Figure 11). Airborne particulate measurements taken aboard the aircraft also showed the symptoms of long-range tranport of air pollution. Nephelometer measurements of light-scattering particulates ranged from relatively high values of about 2×10^{-4} m^{-1} in the late morning to more than 2.5×10^{-4} m^{-1} in the afternoon (Figures 13(a) and (b)). Upwind sulfate and nitrate values were noted to be 64 and 15 ug m^{-3} respectively, among the highest values observed in this study. However, it should be noted that on the southernmost third of the upwind traverse (Figure 12(a) and 13(a)) a broad NO_x plume was encountered, which could well have been a power plant plume from the Windsor-Detroit area, with elevated sulfate and nitrate levels.

Two flights were carried out - the first during the period 11:10 -13:42 EDT, and the second between 16:30 and 19:20 EDT. They will be discussed separately. Traverses were generally at 200-250 m above ground level.

The concurrent aircraft and ground-level observations during the first flight are shown in Figures 12(a) to 12(c). A traverse was carried out upwind of Sarnia shortly before noon (Figure 12(a)), showing relatively high concentrations of ozone and airborne particulates, as has already been noted. An interesting feature of this traverse was the presence of a broad plume (about 35 km wide) apparently due to the Windsor-Detroit area, with ozone concentrations peaking at over 80 ppb and very high concurrent NO_2 levels (NO_x appraoched 30 ppb, while NO was less than 10 ppb). Hydrocarbon concentrations (for species with more than two carbon atoms) were not exceptional in the sample taken during this traverse (about 24 ug m^{-3} total), although the photochemically reactive alkenes did make up a relatively large proportion (10% by weight) of the total.

The observations taken between 1200 and 1400 EDT (Figures 12(b) and (c)) show few additional features in the aircraft data, with the exception of a sharp dip in the ozone data (with concurrent increases in NO_x and light-scattering particulates) which is attributable to the presence of the plume from upwind generating stations near Courtright (see traverse 2). Otherwise the aircraft and ground-level data suggest fairly uniform concentrations in the study area, with no clear evidence of any ozone bulges due to Sarnia. The dip in ozone at the southernmost portions of traverses 3 and 4 is attributable to the generating station plumes, since NO_x values showed an appreciable increase over the same area (Figure 13(a)). It is interesting to note that at 1400 hours a spiral was flown near Kettle Point (see Figure 12(c), approximately where traverse 4 crossed the coastline), between ground level and approximately 1000 m. There was a gradual decrease of ozone with height (from about 128 ppb 70 m above the water surface, to about 80 ppb at 1000 m, Figure 13(a)), but a well-defined ozone bulge was observed between 430 and 600 m, with maximum ozone concentrations slightly in excess of 100 ppb, even though the temperature profile measured by the aircraft indicated neutral conditions. The reason for this bulge is not clear - it may be due to a plume of unknown origin, since it was accompanied by a concurrent slight increase of NO_x, and a more pronounced rise in the light-scattering particulate levels.

The observations during the second flight (1630 to 1920 EDT) are shown in Figures 12(d) and (e). Only aircraft traverses 1 and 2 had any features, notably an apparent ozone plume downwind of the Windsor-Detroit area, which is also suggested by the ground-level data from Thedford and Parkhill. The aircraft data showed high levels of light-scattering particulates in this plume (b_{scat} as high as $4 \times 10^{-4}\ m^{-1}$), although NO_x levels were near instrument detection limits (Figure 13(b)). The upwind hydrocarbon sample, collected during traverse 1, had high hydrocarbon levels (88 ug m^{-3}) primarily due to aromatics (which made up 82% of the total). The one filter pack sample collected on this flight, downwind of Sarnia, gave very high sulfate concentrations (126 ug m^{-3}), due to an apparent sampling of the generating station plumes during traverse 2 -which also explains the dip in ozone levels downwind of Courtright. Two additional traverses were flown at about 100-120 km to the northeast of Sarnia, but these were generally without any features, and are not shown in Figure 12(e).

It should be noted that, with the exception of the upwind sample collected during the first flight of July 3, all aircraft hydrocarbon samples indicated high aromatic levels (in the 57-79 ug m^{-3} range) due particularly to the xylenes. It is not clear if these unusually high values are genuine, or the result of an unknown source of contamination. A comparison of the aircraft samples, collected after 1230 on July 3, with concurrent hydrocarbon samples collected at both Camlachie and Courtright, showed much higher aromatic levels in the aircraft data. Since a "fingerprint" sample collected in the Huron Aviation hangar also showed relatively high aromatic (and xylene) levels, contamination of this particular set of samples is suspected.

Sampling for formaldeyhde was carried out throughout the day at Camlachie, where late morning and early afternoon levels in the 3-7 ppb range were observed. The TAGA unit at Courtright reported a set of measurements for other aldehydes, Ketones, acetates and alcohols collected around 1000 hours. For these compounds values were not far above detectable limits, with the exception of propanal (4.9 ppb), butanal (1.5 ppb) and methyl-ethyl ketone (1.2 ppb).

Thus, on July 3 - an example of high ozone levels developing under a "back-of-the-high pressure system" synoptic condition, and accompanied by high atmospheric sulfate levels and haziness - there was no evidence of an ozone buildup downwind of Sarnia, although an ozone plume attributable to the Windsor-Detroit area was suggested in the data. The ozone levels measured throughout southwestern Ontario are clearly largely due to long-range transport. A survey of the ground-level measurements of pollutants other than ozone in the area - especially the early morning hydrocarbon and NO_x levels - generally showed values comparable to the monthly means, with the interesting exception that Camlachie, which was approximately downwind of Sarnia, registered high levels of hydrocarbons, especially alkanes and aromatics (benzene and toluene) in the measurements made before noon (C_3 and higher hydrocarbons of 108-196 ug m^{-3}; alkane levels of 62-151 ug m^{-3}; aromatic levels of 28-39 ug m^{-3}). These measurements are appreciably higher than the "upwind" observations at Courtright (which had relatively high alkane levels, 43-59 ug m^{-3} during the same period, but aromatics less than 11 ug m^{-3}), and are probably due to Sarnia emissions. Despite this, ozone levels attributable to Sarnia could not be detected in the survey area. This may be due to the observed dominance of the relatively slow-reacting benzene and alkanes in the Sarnia emissions. Sampling was only carried out to an air parcel travel time of about 2-4 hours, and appreciable ozone formation may not have taken place yet. Unfortunately, data from the ozone precursor monitor at the downwind Camlachie site were unavailable during this time, so the low potential for oxidant formation in the Sarnia emissions, suggested by the absence of downwind ozone accumulation on this day, could not be confirmed independently by the ozone precursor data. NO_x levels at the MOE mobile laboratory at Camlachie were below detection limits, while no data were available from the York University NO analyzer.

TIME VS. OZONE CONCENTRATION

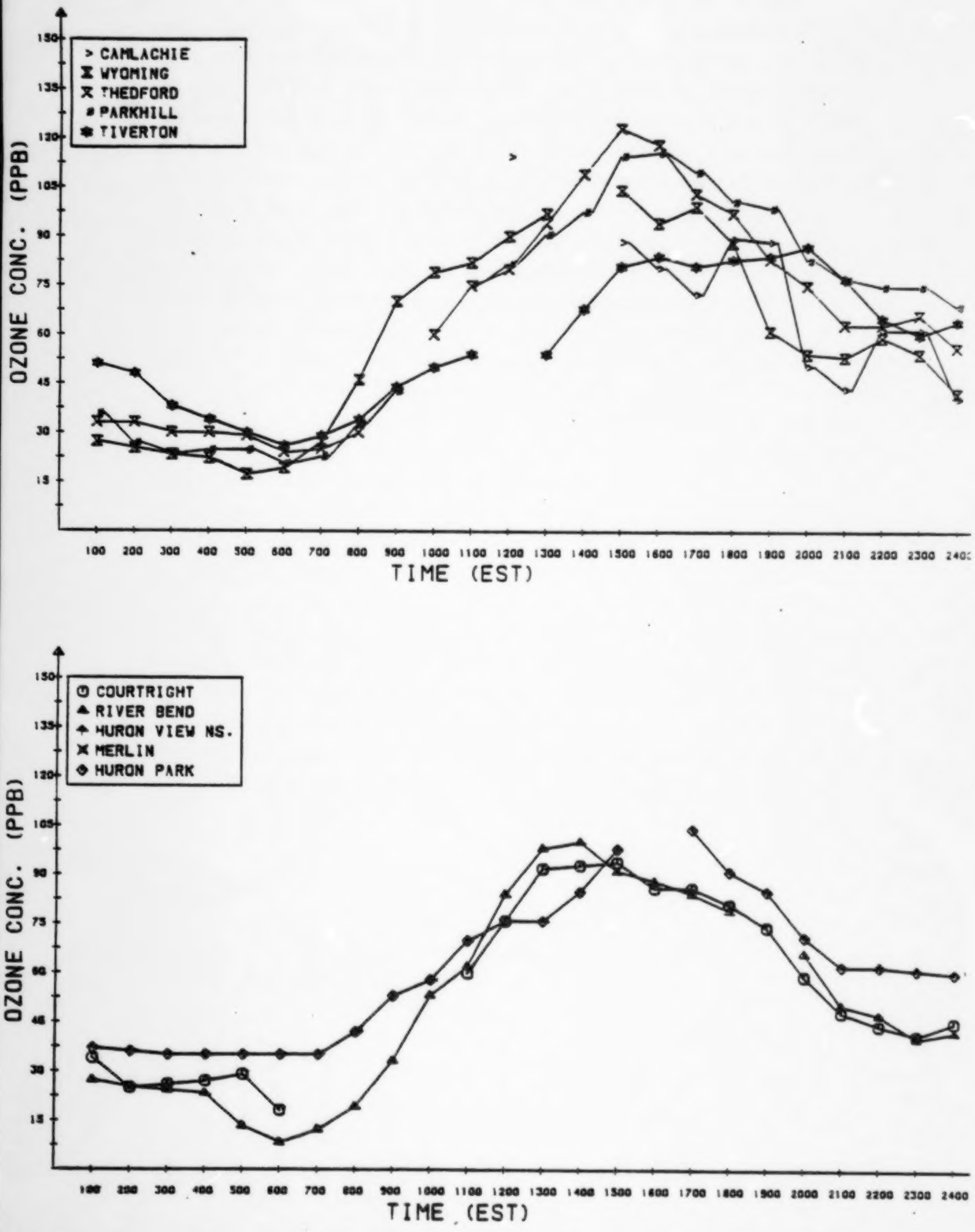


Figure 11: Diurnal Variation of Ozone Concentrations in the Sarnia Area, July 3

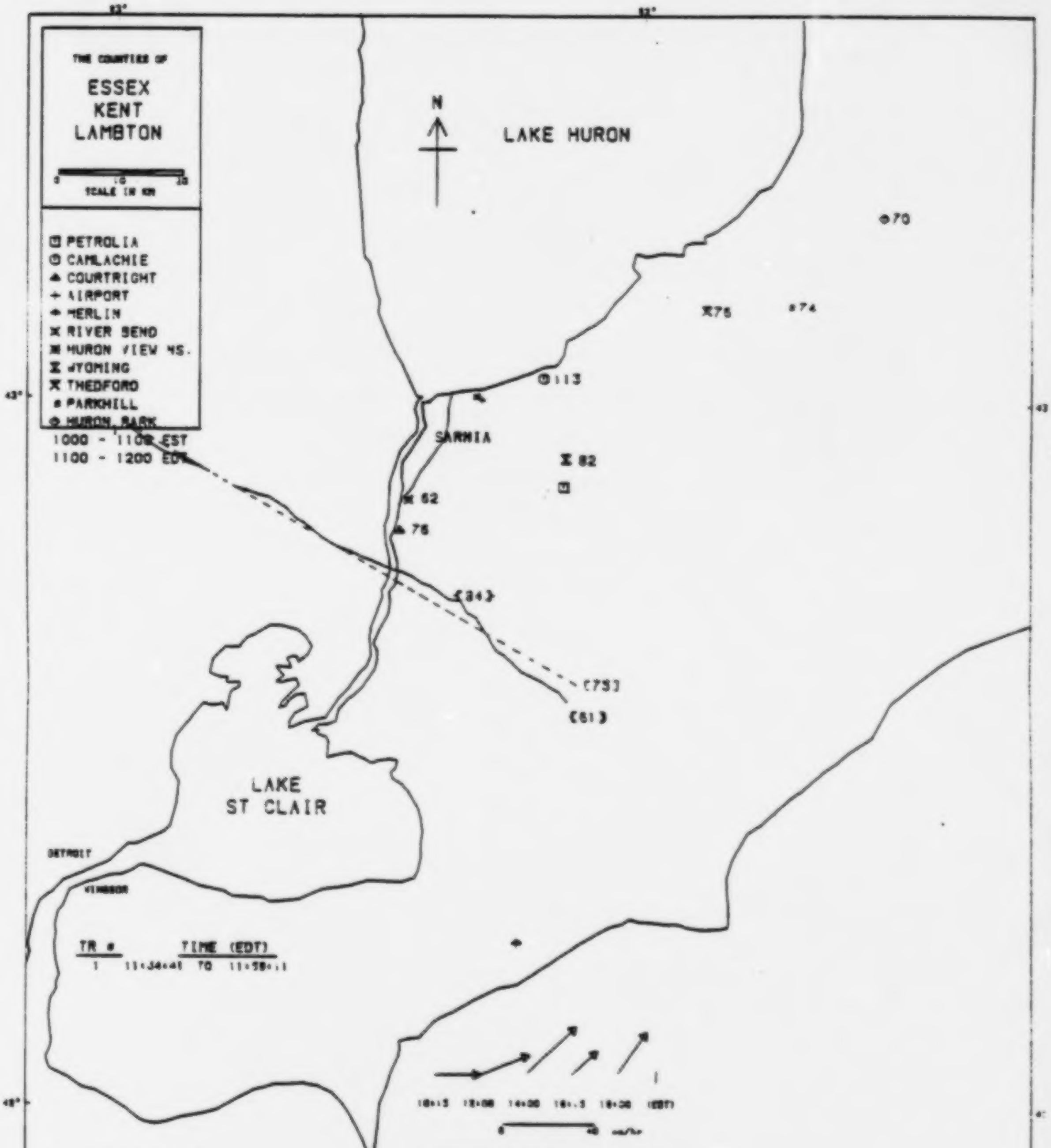

ESSEX
KENT
LAMBTON
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW HS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
1000 - 1100 EST
1100 - 1200 EDT
N
LAKE HURON
SARNIA
70
75
74
113
82
62
76
(84)
(75)
(61)
LAKE ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
1
TO
LAKE ERIE

Figure 12(a): Ozone Observations in the Sarnia Area on July 3, 11-12 EDT

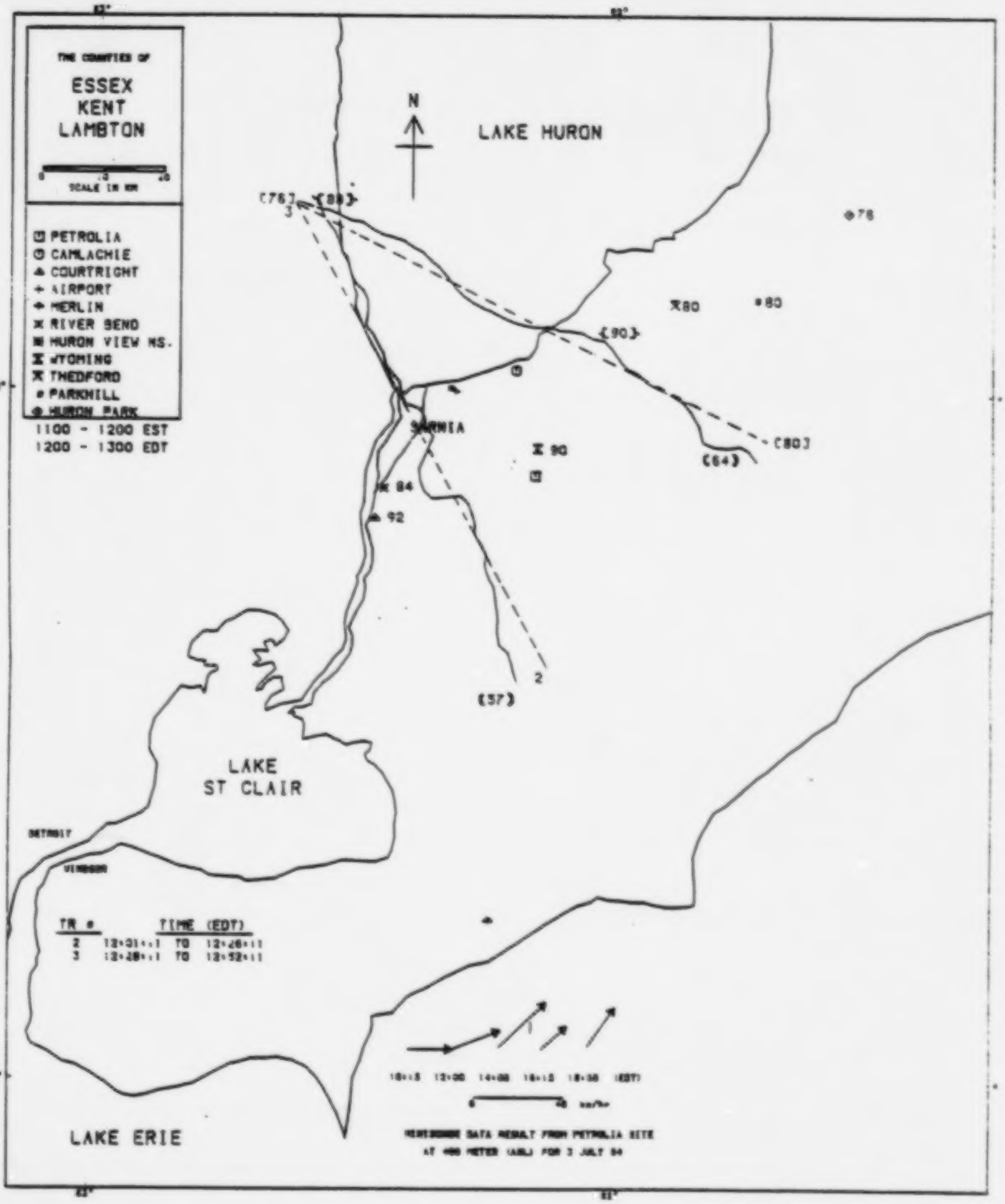

THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
20
40
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW HS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
1100 - 1200 EST
1200 - 1300 EDT
N
LAKE HURON
[76]
[89]
3
76
80
80
[90]
[80]
[64]
SARNIA
90
84
92
2
[57]
LAKE ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
2
12:01:11 TO 12:26:11
3
12:28:11 TO 12:52:11
(EDT)
km/hr
LAKE ERIE

Figure 12(b): Ozone Observations in the Sarnia Area on July 3, 12-13 EDT

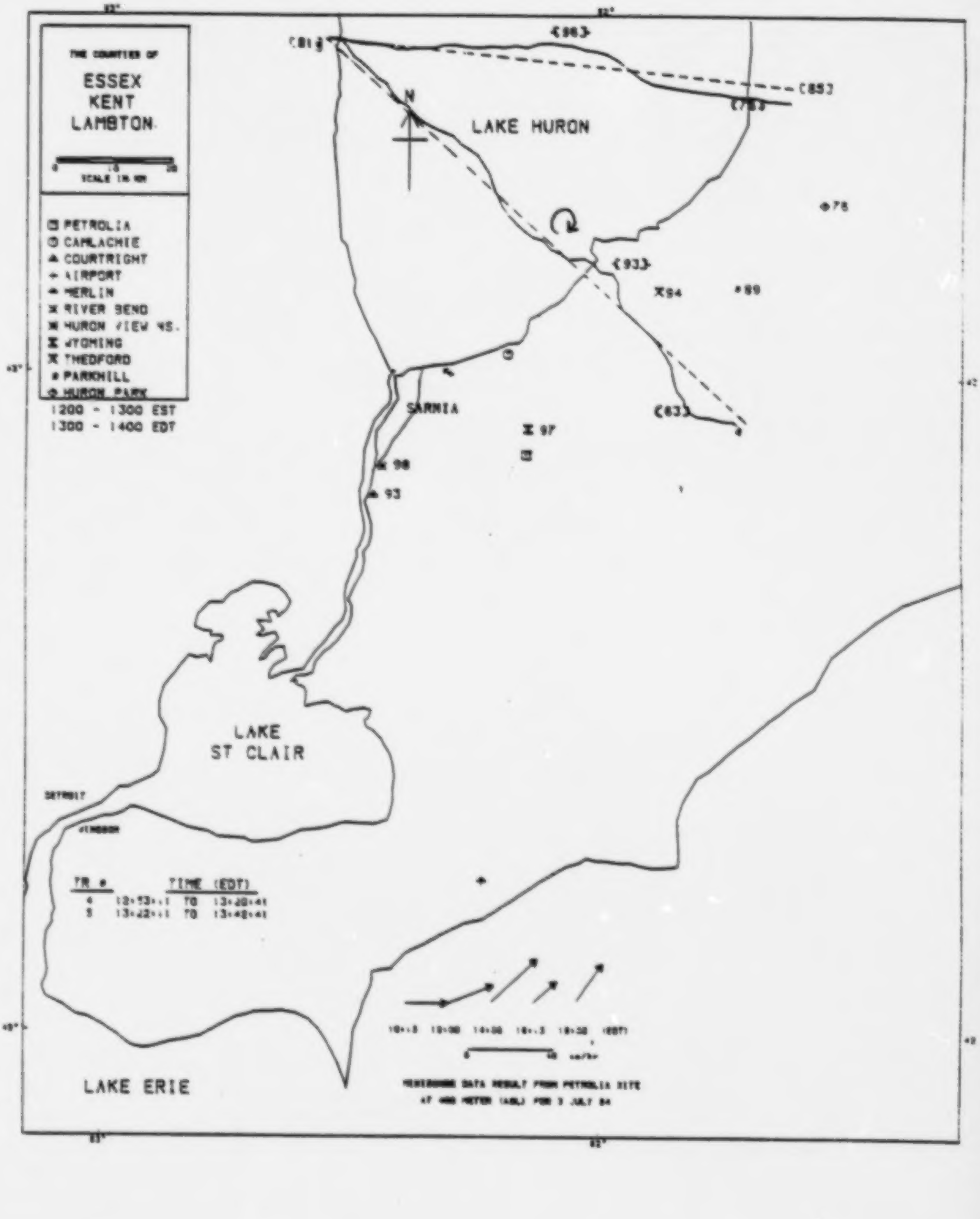

THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW HS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
1200 - 1300 EST
1300 - 1400 EDT
N
(81)
(86)
(85)
(75)
LAKE HURON
76
(93)
94
89
(63)
SARNIA
97
98
93
LAKE
ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
(EDT)
0
LAKE ERIE

Figure 12(c): Ozone Observations in the Sarnia Area on July 3, 13-14 EDT

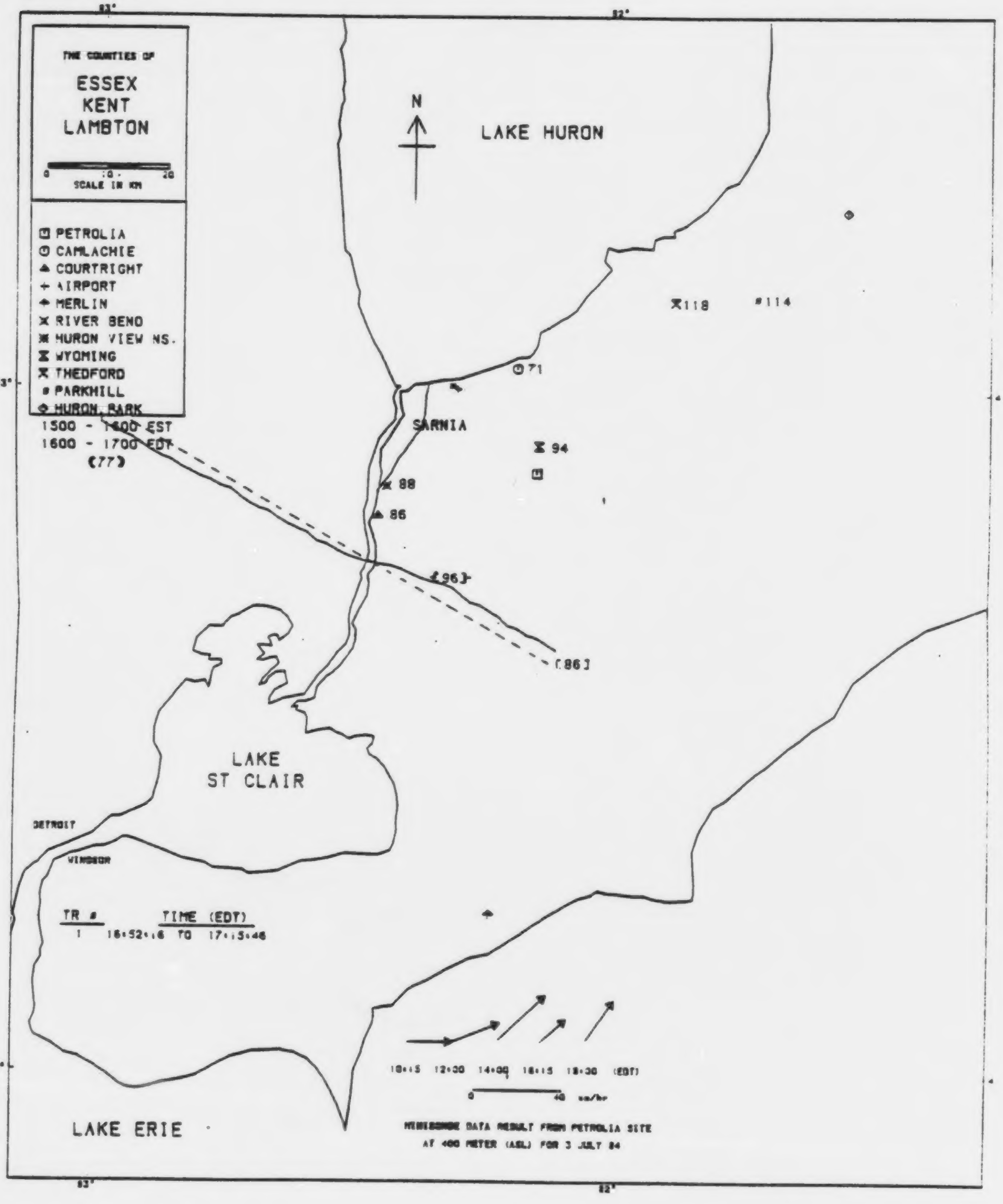

83°
82°
THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
N
LAKE HURON
118
114
71
43°
SARNIA
94
1500 - 1600 EST
1600 - 1700 EDT
(77)
88
86
(96)
(86)
LAKE
ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
1
16:52:16 TO 17:15:46
10:15
12:30
14:00
16:15
18:30
(EDT)
0
40
km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 400 METER (ASL) FOR 3 JULY 84
42°
LAKE ERIE

Figure 12(d): Ozone Observations in the Sarnia Area on July 3, 16-17 EDT

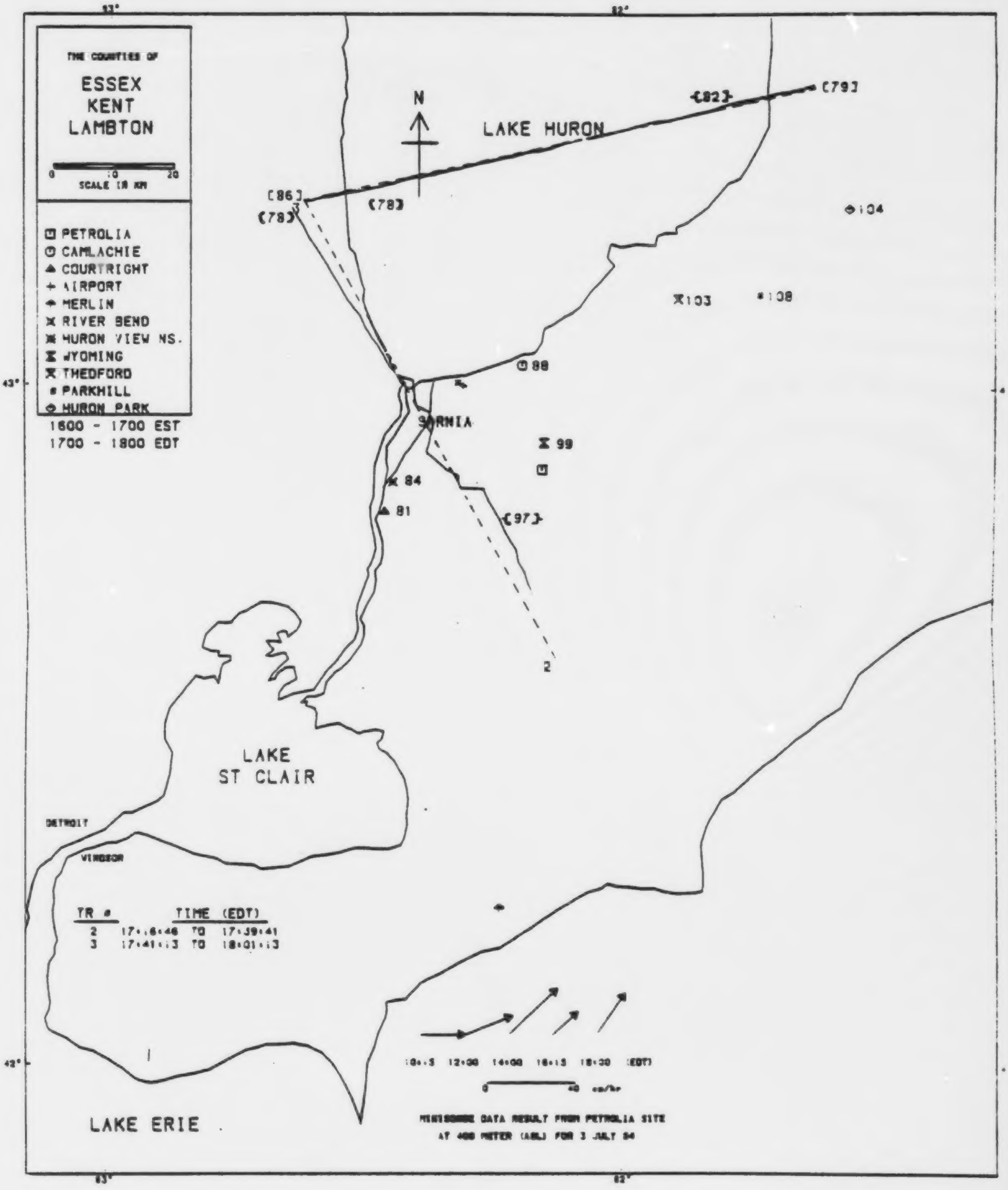

83°
82°
THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
1600 - 1700 EST
1700 - 1800 EDT
N
LAKE HURON
[82]
[79]
[86]
[78]
[78]
3
104
103
108
88
43°
SARNIA
99
84
81
[97]
2
LAKE
ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
2 17:16:46 TO 17:39:41
3 17:41:13 TO 18:01:13
10:15
12:00
14:00
16:15
18:30
(EDT)
0
40
km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 400 METER (AGL) FOR 3 JULY 84
42°
LAKE ERIE

Figure 12(e): Ozone Observations in the Sarnia Area on July 3, 17-18 EDT

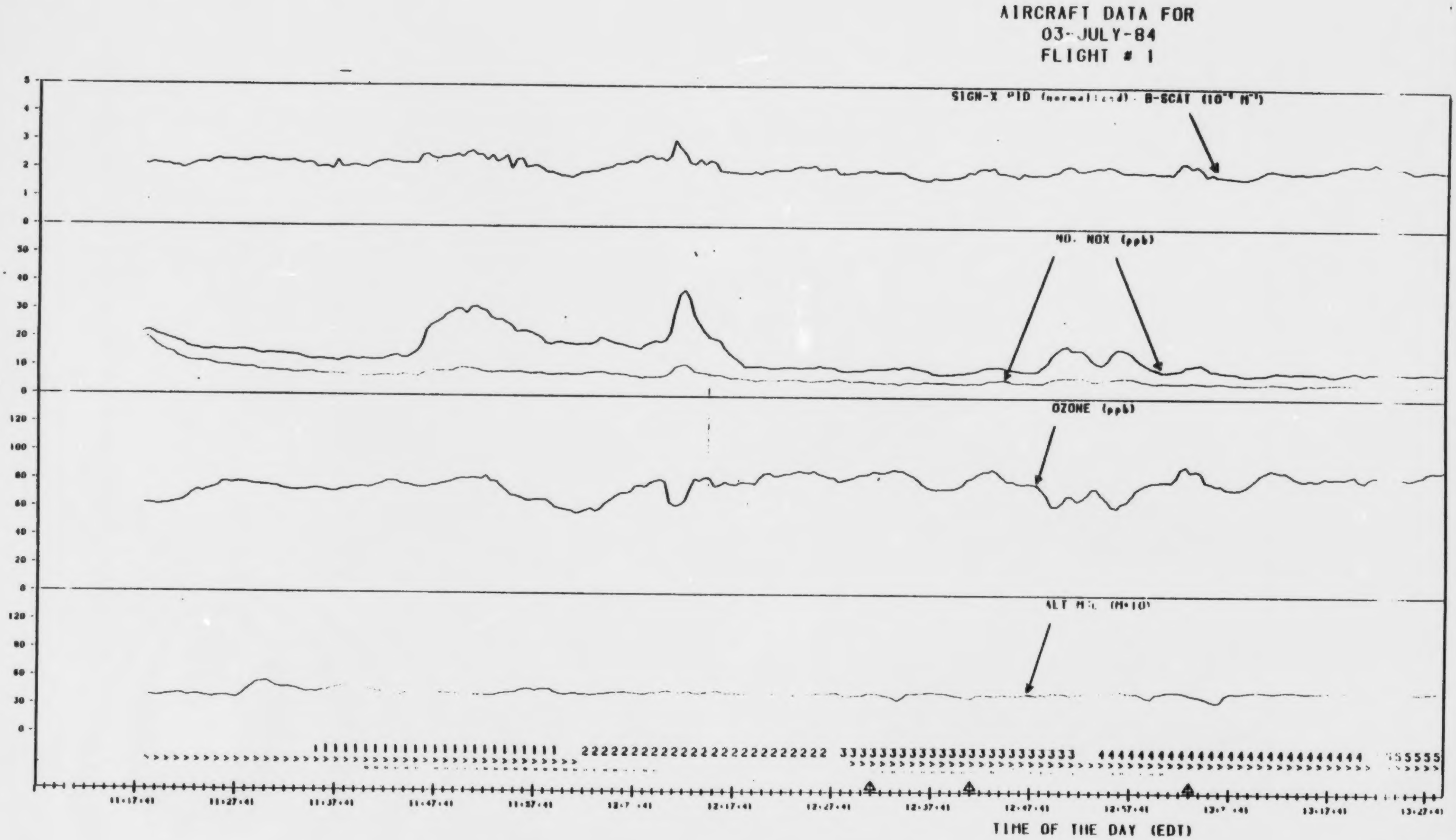


Figure 13(a): Aircraft Observations on July 3, 11-14:30 EDT

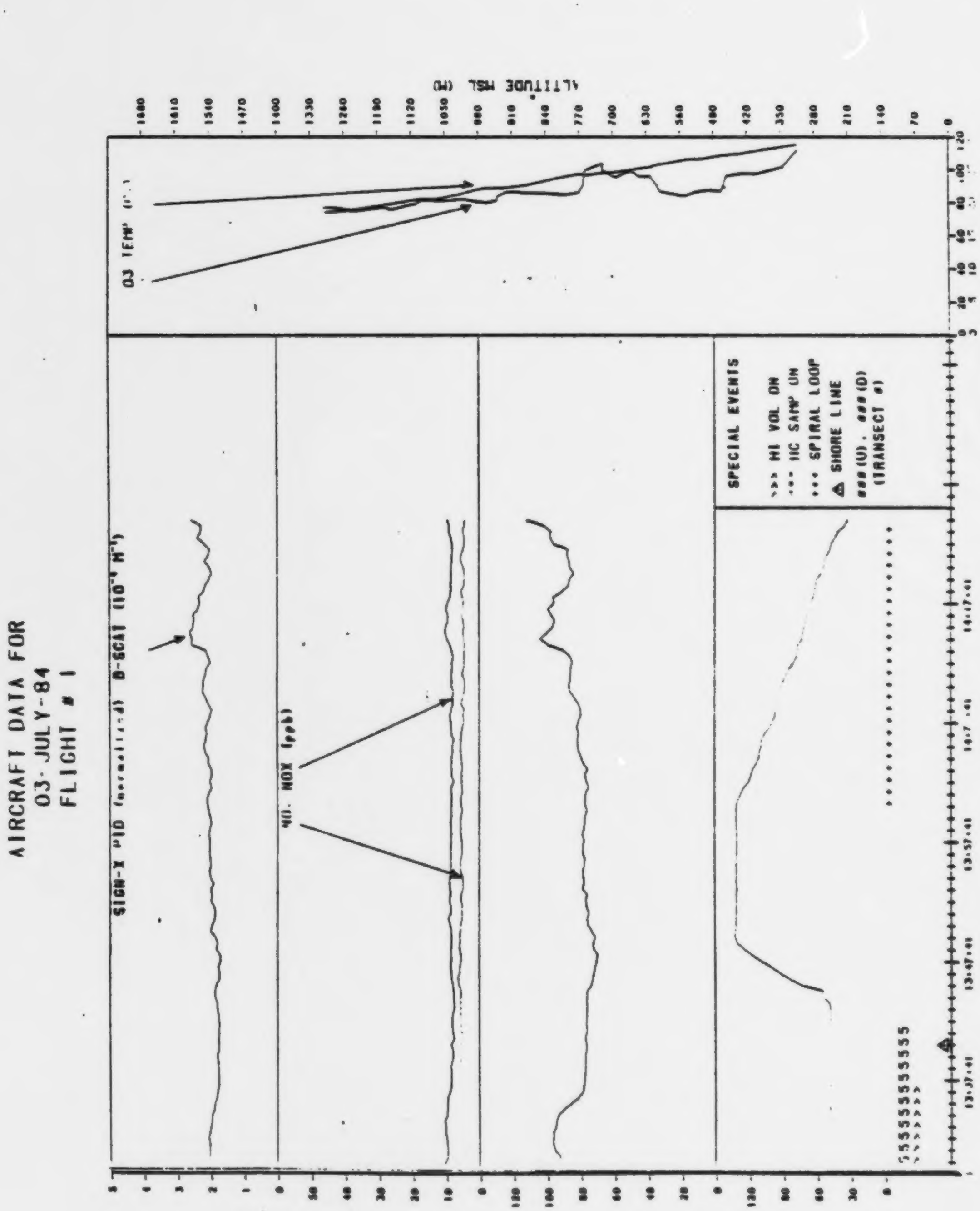


Figure 13(a): Aircraft Observations on July 3, 11-14:30 EDT (continued)

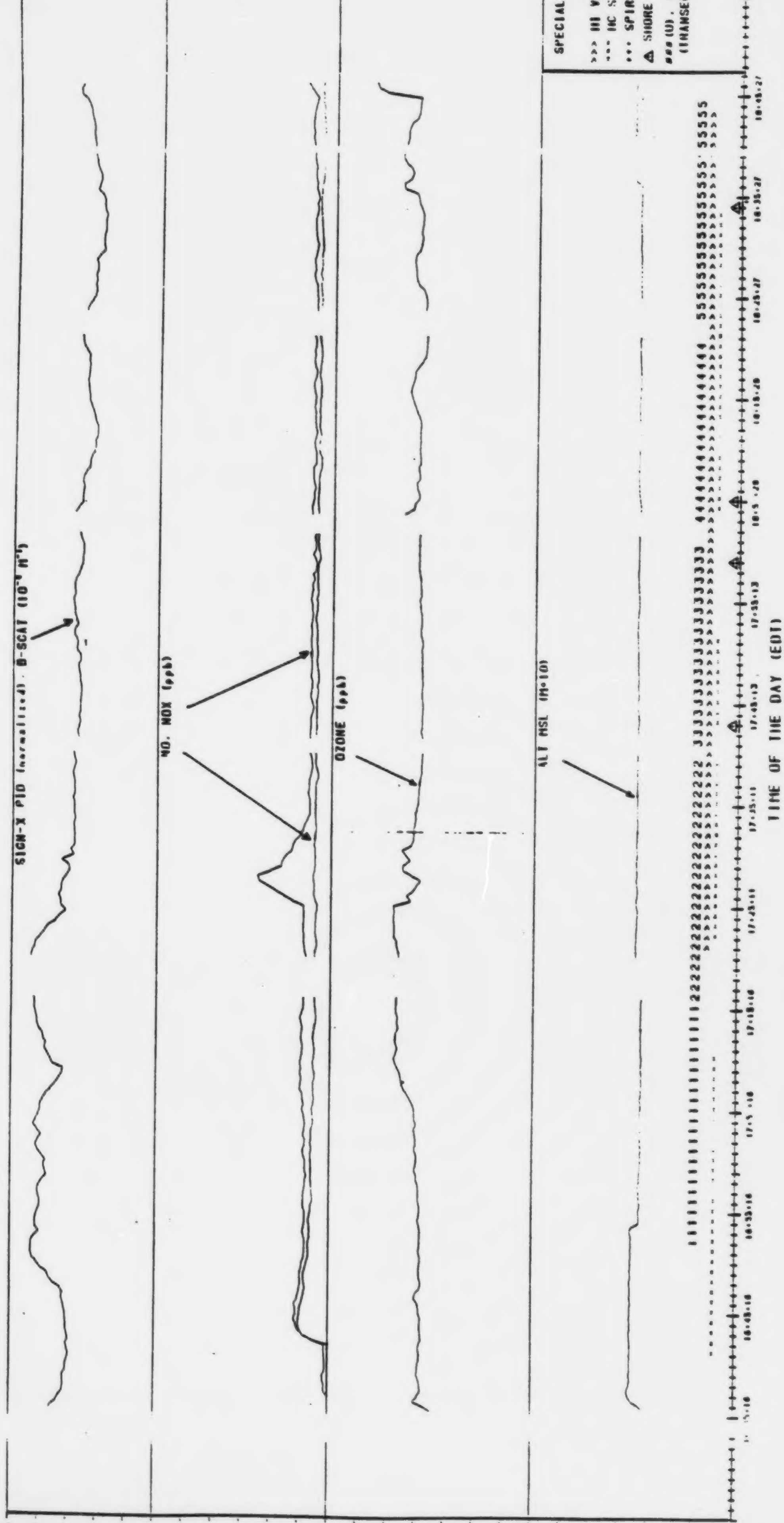


Figure 13(b): Aircraft Observations on July 3, 16-19 EDT

3.4 July 5

A slow-moving NE-SW cold frontal system tracked across the lower Great Lakes on July 5. This resulted in light and variable surface winds with early morning fog and a wind shift from S-SW to N by mid-morning, and wind speeds typically in the range 5 to 10 km h^{-1}. During the period of interest (0900-100 EDT), northerly surface winds were noted, although at the airplane sampling height, winds had a west-southwesterly component. Broken to overcast skies prevailed, with temperatures near $20^{\circ}C$, and surface relative humidities in the 60-70% range. The hourly average total solar radiation was below 70 milliwatts per cm^2. Minisonde data collected at Camlachie and Petrolia during the period 0900-1300 EDT suggest an initial mixed layer height of about 200 m, increasing to 400-500 m by 1200 EDT, and decreasing slightly thereafter.

Backward trajectories of air parcels over the Sarnia area during the study period indicate slow movement from Illinois northeastwards to lower Lake Michigan and then eastward. Forward trajectories from Sarnia show an eastward movement.

Ozone levels across the study area on this day were relatively low, building up to about 50-60 ppb at most stations by mid-afternoon (see Figure 14).

The aircraft traverses were carried out at a height of about 270 m above ground level. The upwind traverse (Figure 15(a)) indicated fairly uniform ozone levels of about 40-45 ppb, but at the same time, the presence of a pollution plume roughly south of Lake Huron, with relatively high NO_x (10-20 ppb) and light-scattering particulate (b_{scat} up to 2×10^{-4} m^{-1}) levels (outside of this plume, NO_x and b_{scat} values were less than 10 ppb, and about 0.5×10^{-4} m^{-1}, respectively) - see Figure 16. The high-volume filter pack data support these observations, since upwind sulfates, nitrates and sulfur dioxide were relatively high (75, 8 and 46 ug m^{-3} respectively). This plume could also be detected in the downwind data out to the farthest traverse flown, and a spiral over Lake Huron, near Kettle Point, indicated that it was confined to the mixing layer. Most of the other (relatively weak) features in the downwind aircraft data (Figures 15(a) and (b)) can be attributed to this "upwind" plume, as well as to scavenging by the

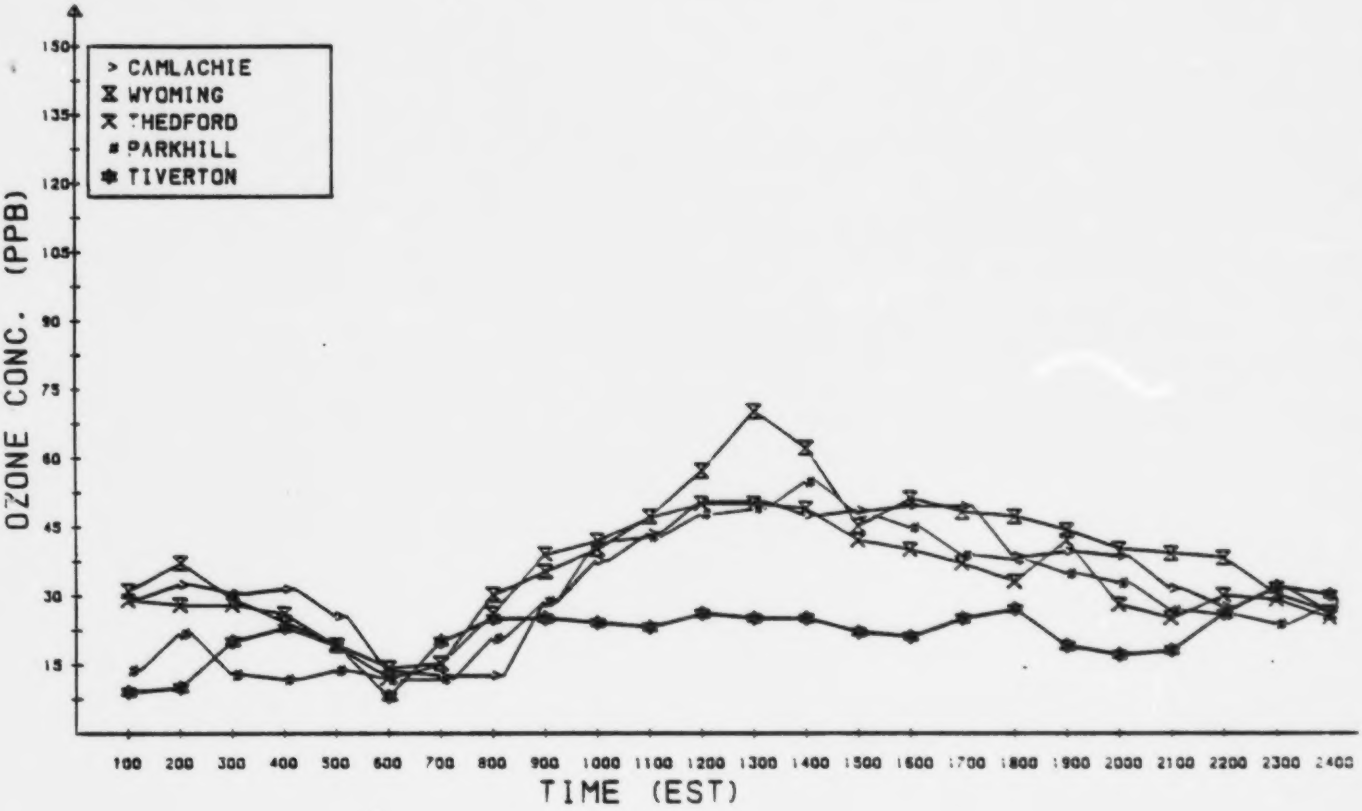
NO_x emissions from the generating stations near Courtright. However, meteorological interpretation of the data is difficult, due to the light and variable winds on this day. The spiral near Kettle Point showed a gradual ozone decrease from 50-60 ppb at about 60 m above the lake to 40 ppb at 1200 m. There was no evidence for any clear ozone plume attributable to Sarnia, or any other upwind sources for that matter. It is interesting to note that during this period, as on several other occasions, the ground-level monitoring station at Merlin (about 80 km south of Sarnia) showed appreciably lower ozone levels (less than 26 ppb) than the stations to the east of Sarnia on Figures 15(a) and (b), which were in the 40-60 ppb range. However, the aircraft traverses (especially upwind of Sarnia) suggest that this difference is not due to Sarnia emissions.

The hydrocarbon levels in the area, measured at Courtright and Camlachie, were relatively high (especially at the former location, where total C_3 and greater hydrocarbon concentrations as high as 170 ug m^{-3} were reported), probably as a result of the light and variable winds, and consisted largely of alkanes (about 70-80%), with aromatics accounting for most of the rest of the total hydrcarbon concentration. Nitrogen oxides were also relatively high at Courtright (up to about 50 ppb during the period of interest), but non-detectable at Camlachie. It is interesting to note that, despite these differences in nitrogen oxides levels, the ozone precursor monitors at both locations gave comparable results (about 15 ppb ozone).

The aircraft hydrocarbon samples (about 50 ug m^{-3} upwind, 85 ug downwind) were found to contain only alkanes and aromatics - the upwind sample having these compounds in comparable proportions; the downwind sample being dominated (about 70%) by aromatics, primarily 0 -and m- xylene.

It is of interest that there were two subsequent days on this survey (July 8 and 13, see below) with light and variable winds, and relatively high hydrocarbon levels in the area. On both of these, a Sarnia contribution to the ozone concentrations was found. The main meteorological feature distinguishing July 5 from these days seems to be the lower solar radiation due to overcast skies, and slightly lower surface temperatures.

TIME VS. OZONE CONCENTRATION



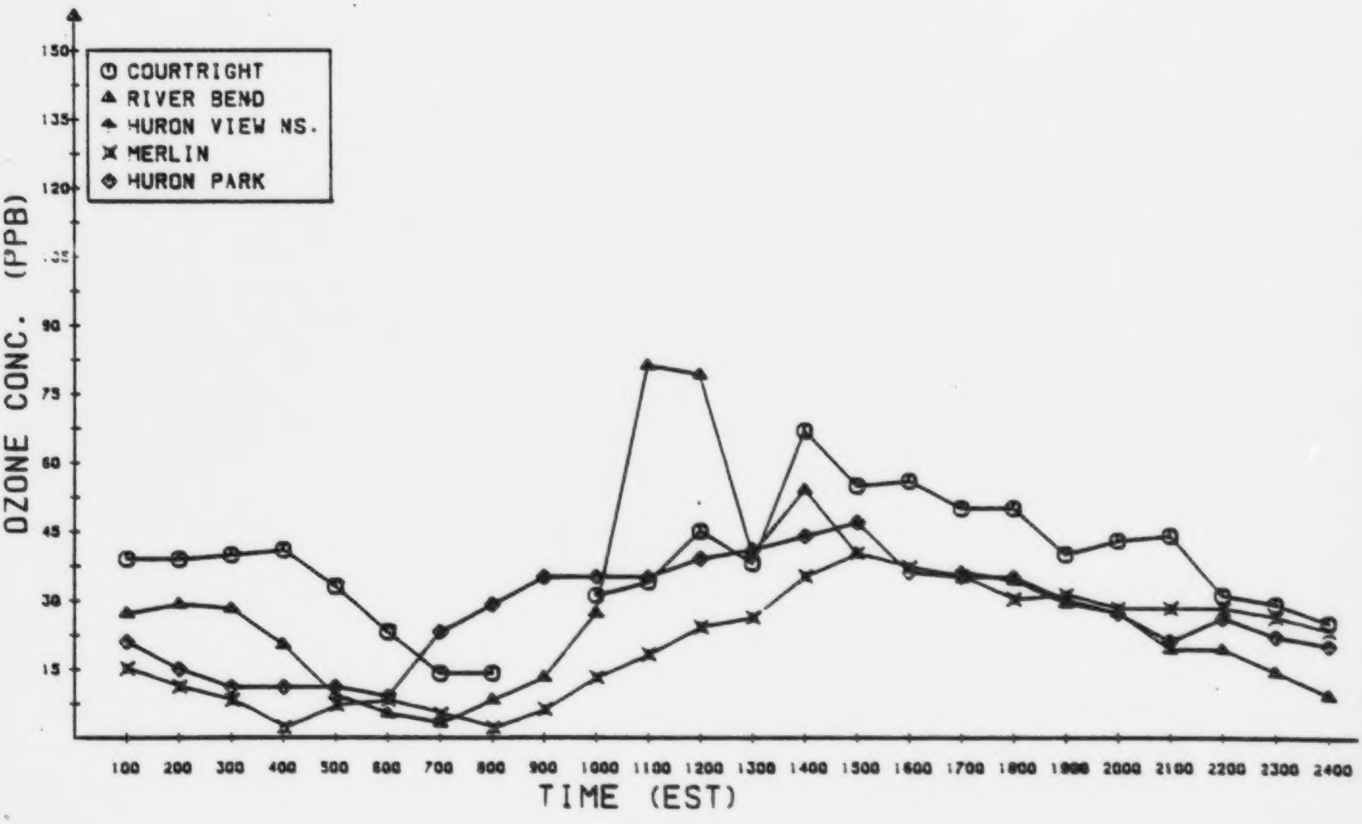


Figure 14: Diurnal Variation of Ozone Concentrations in the Sarnia Area, July 5

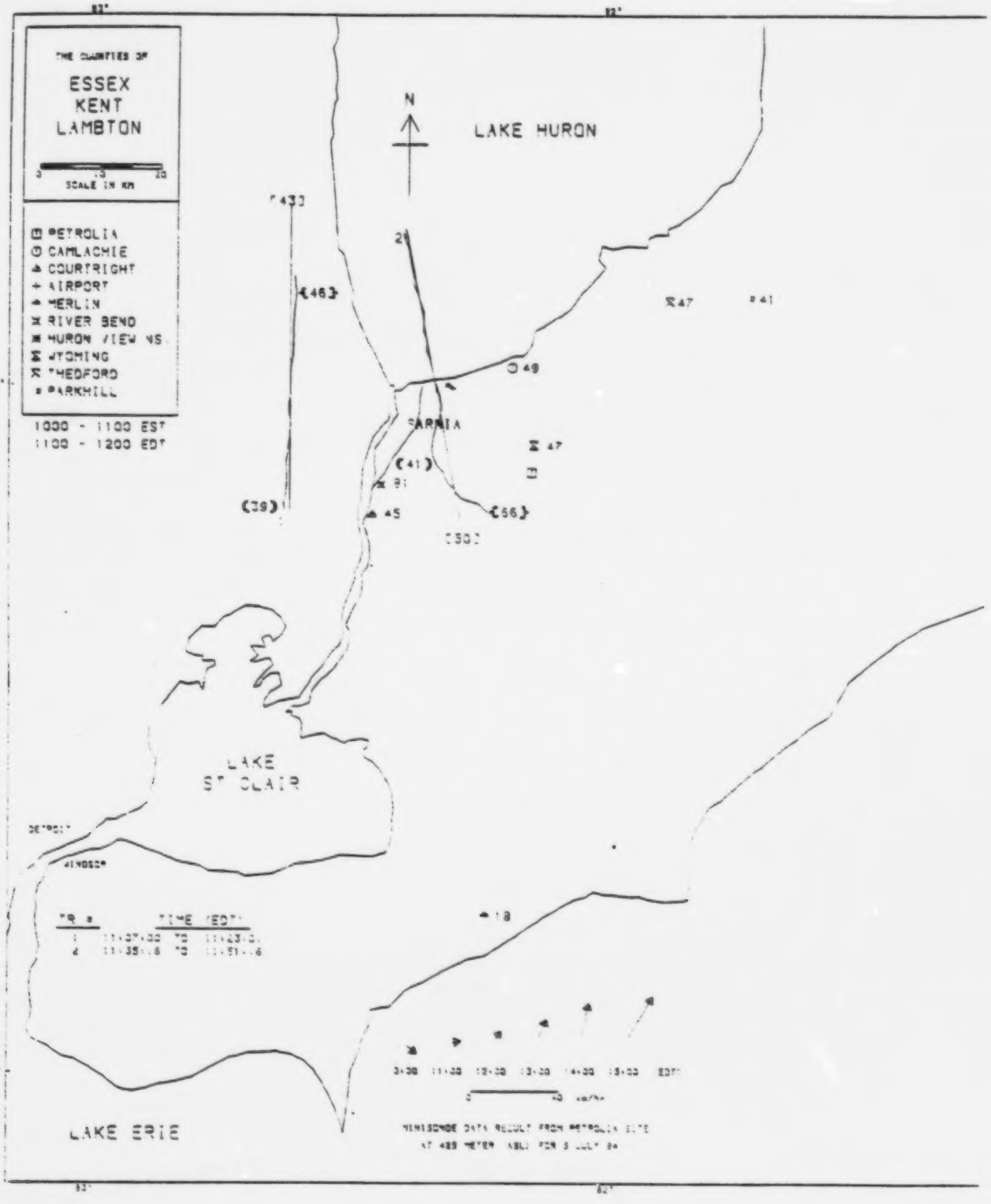

83°
82°
THE COUNTIES OF
ESSEX
KENT
LAMBTON
0 10 20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS.
WYOMING
THEDFORD
PARKHILL
1000 - 1100 EST
1100 - 1200 EDT
N
LAKE HURON
[43]
{46}
(39)
2
47
41
49
SARNIA
47
(41)
31
45
{56}
[50]
43°
LAKE ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
1 11:07:00 TO 11:23:0.
2 11:35:16 TO 11:51:16
18
10:00 11:00 12:00 13:00 14:00 15:00 EDT
0 40 km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 485 METER (ASL) FOR 5 JULY 84
LAKE ERIE
42°
83°
82°

Figure 15(a): Ozone Observations in the Sarnia Area on July 5, 11-12 EDT

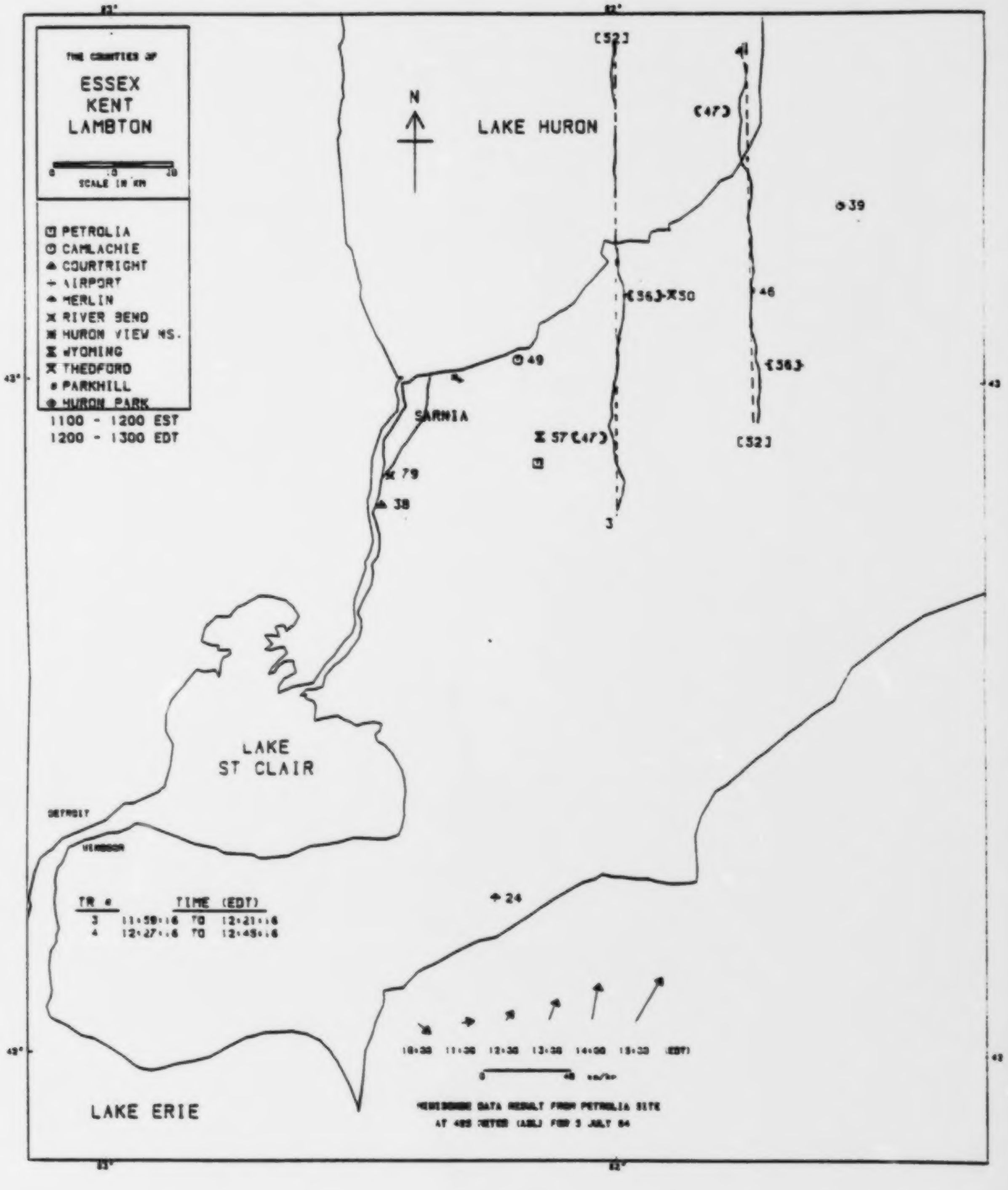

THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW HS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
1100 - 1200 EST
1200 - 1300 EDT
N
LAKE HURON
SARNIA
LAKE ST CLAIR
DETROIT
WINDSOR
LAKE ERIE
[52]
41
[47]
39
[56]
50
46
[56]
49
57
[47]
[52]
79
38
3
24
TR #
TIME (EDT)
3 11:59:16 TO 12:21:16
4 12:27:16 TO 12:45:16
10:30
11:30
12:30
13:30
14:00
15:30
(EDT)
0
48
km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 485 METER (ASL) FOR 5 JULY 84
83°
82°
43°

Figure 15(b): Ozone Observations in the Sarnia Area on July 5, 12-13 EDT

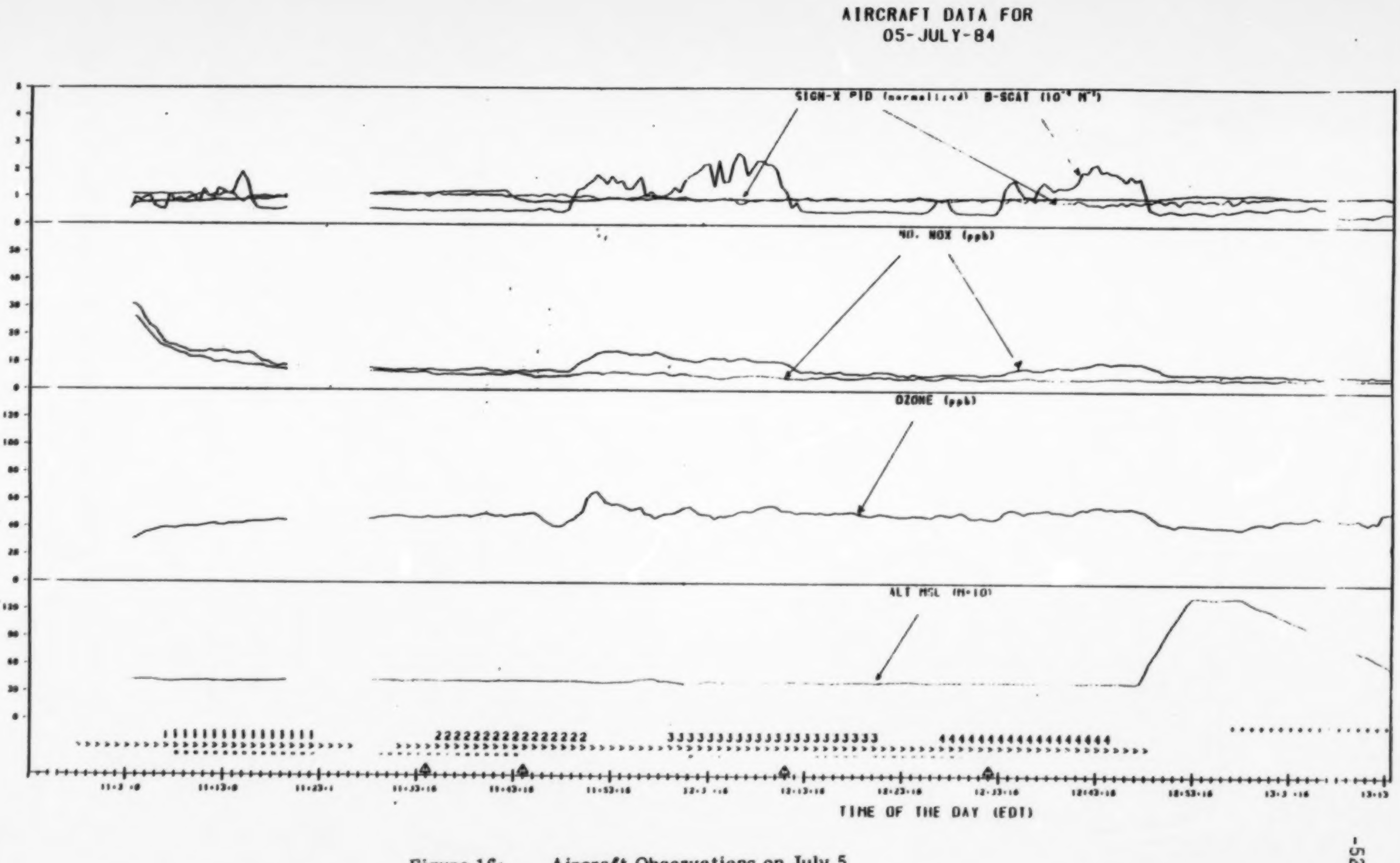


Figure 16: Aircraft Observations on July 5

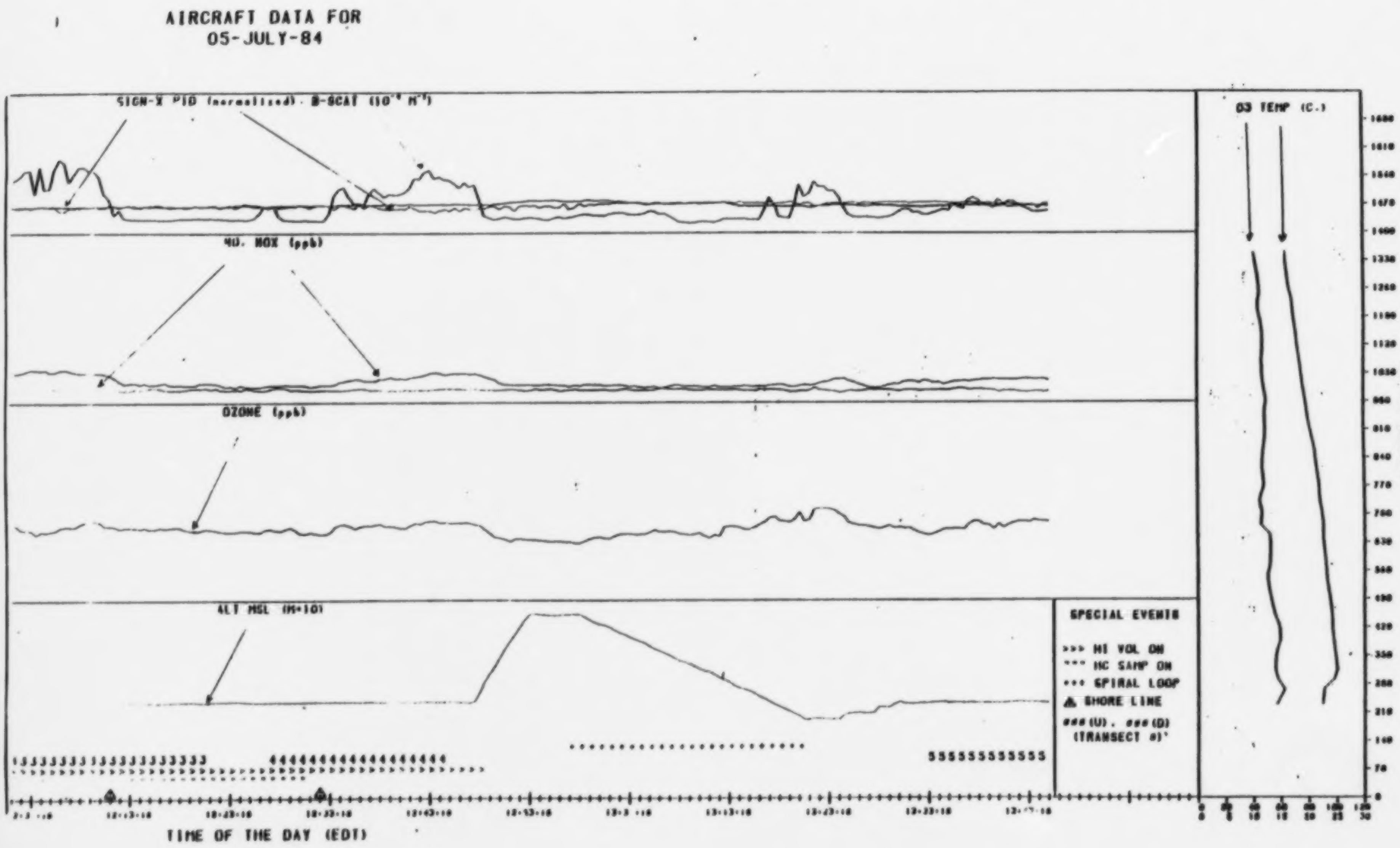


Figure 16: Aircraft Observations on July 5 (continued)

3.5 July 7

On July 7, the study area came under the influence of a low pressure system which was originally centered just to the east of James Bay, and moved slowly northeastward through the day: NW flows were experienced behind the cold front associated with this low. During the period of interest (0900-1400 EDT) winds were generally W-NW, with speeds in the 20-25 km h^{-1} range. Cloudy skies prevailed with somewhat cool conditions (temperatures in the 13-18°C range), relative humidities of 50-60%, and solar radiation less than 60 milliwatts cm^{-2}. The minisonde data suggest patchy mixing layers in the morning at less than 700 m, and generally stable conditions in the afternoon.

Backward trajectories of air parcels over the Sarnia area during the study period indicate a path from northern Ontario southward through central Lake Superior and then southeastward to Sarnia. Forward trajectories from Sarnia indicate a southeasterly path during the period of interest.

As expected from the air parcel's previous history and the prevailing meteorological conditions, ozone levels across the study area were low (less than about 40 ppb - see Figures 17 and 18(a) to (e)). The air was also quite clean in other respects: visibility was good, with nephelometer b_{scat} values at less than 0.5×10^{-4} m^{-1} - see Figure 19. The aircraft's high-volume filter pack sulfate and nitrate values, determined on traverses 1 and 2 upwind of Sarnia (Figure 18(a)), were low, at 6 and 0.8 ug m^{-3} respectively. Nitrogen oxides on all monitoring platforms were at detection limits, except for the high-sensitivity NO analyser at Camlachie, where values of 0.5 ppb or less are reported during the period of interest. No formaldehyde or hydrogen peroxide values were reported on this day, but TAGA observations of other aldehydes and ketones generally gave sub-ppb concentrations, with many values below detection limits. Hydrocarbon levels at Camlachie and Courtright were very low (total non-methane hydrocarbons less than 13 and 26 ug m^{-3} respectively), but the aircraft levels were somewhat higher (42-58 ug m^{-3}), largely due to alkyl benzenes. Contamination of the samples is strongly suspected, since even the apparent upwind levels were high (non-methand hydrocarbons, 58 ug m^{-3}; alkanes, 18 ug m^{-3}; aromatics 40 ug m^{-3}). Ozone precursor monitor results at Camlachie and Courtright were below detection limits during the measurement period.

The aircraft sampling was carried out at about 270 m, and the ozone results are shown in Figures 18(a) to (e). As can be seen, there are few features in the data, with ozone levels low and uniform across the study area, and in general agreement with the ground-level ozone observations.

JULY 7

TIME VS. OZONE CONCENTRATION

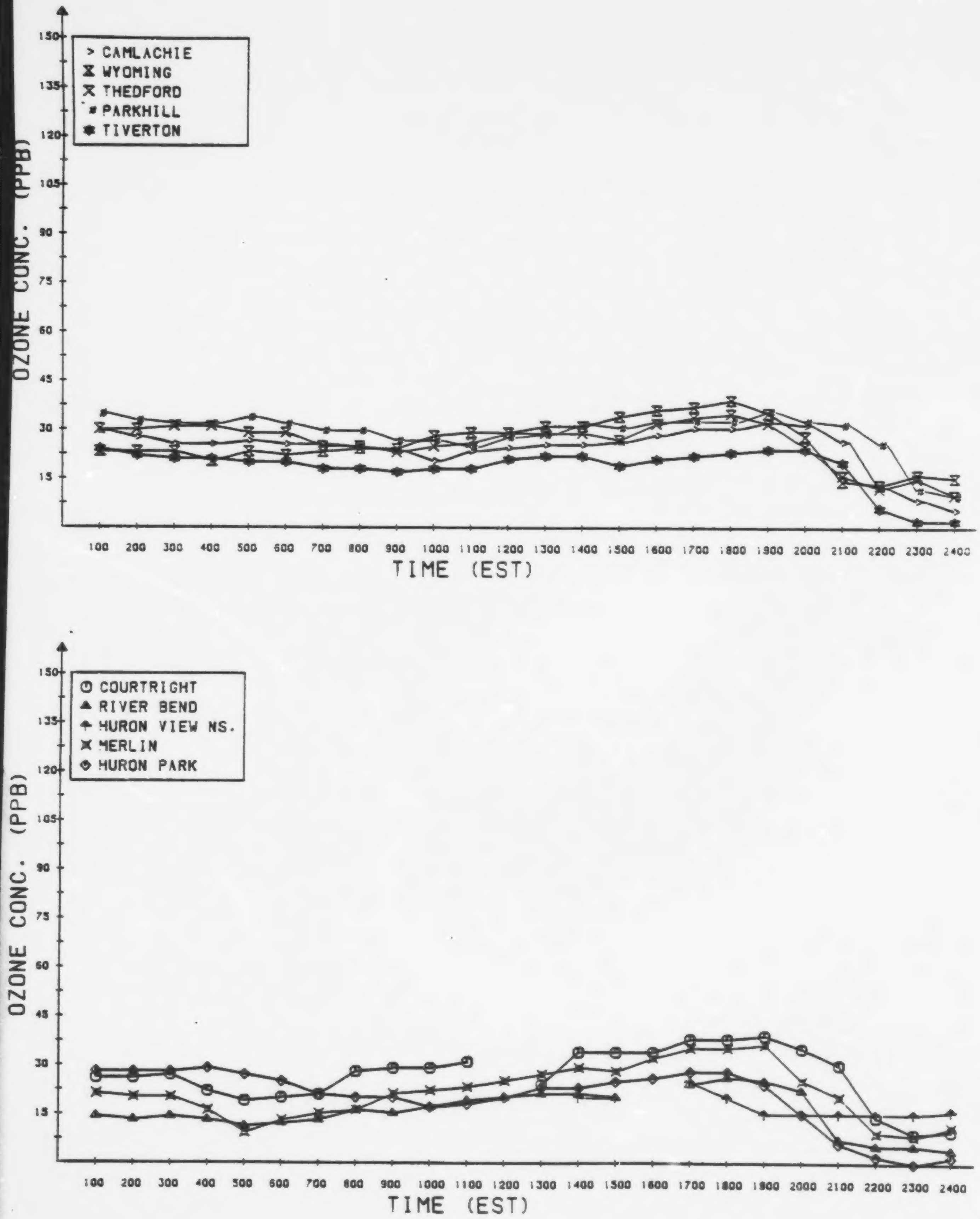


Figure 17: Diurnal Variation of Ozone Concentrations in the Sarnia Area, July 7

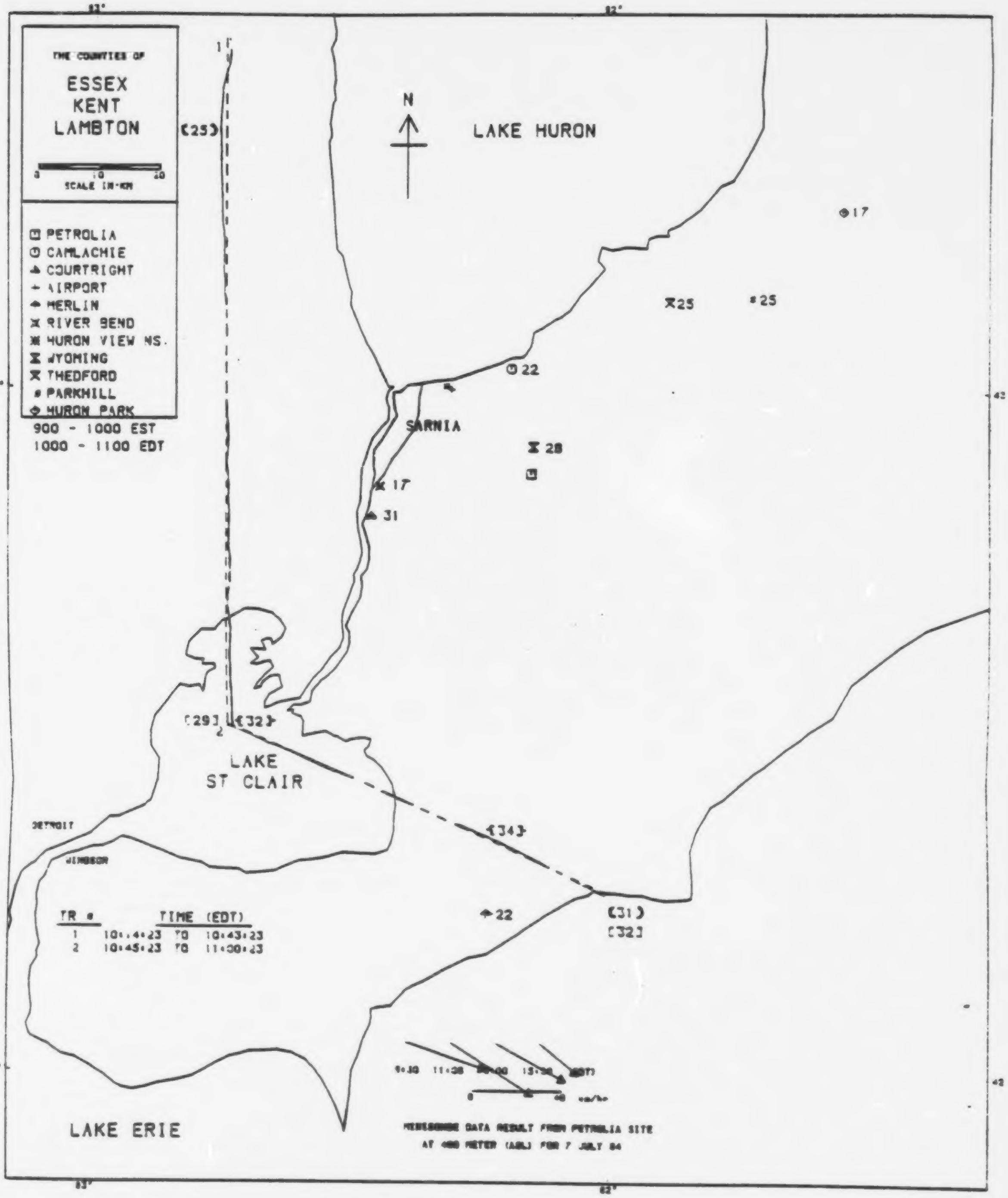

83°
82°
THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
900 - 1000 EST
1000 - 1100 EDT
1
[25]
N
LAKE HURON
17
25
25
22
43°
SARNIA
28
17
31
[29]
2
[32]
LAKE
ST CLAIR
DETROIT
WINDSOR
[34]
TR #
TIME (EDT)
1 10:14:23 TO 10:43:23
2 10:45:23 TO 11:00:23
22
[31]
[32]
9:30
11:30
15:30
(EDT)
0
40
km/hr
DATA RESULT FROM PETROLIA SITE
METER (AGL) FOR 7 JULY 84
42°
LAKE ERIE

Figure 18(a): Ozone Observations in the Sarnia Area on July 7, 10-11 EDT

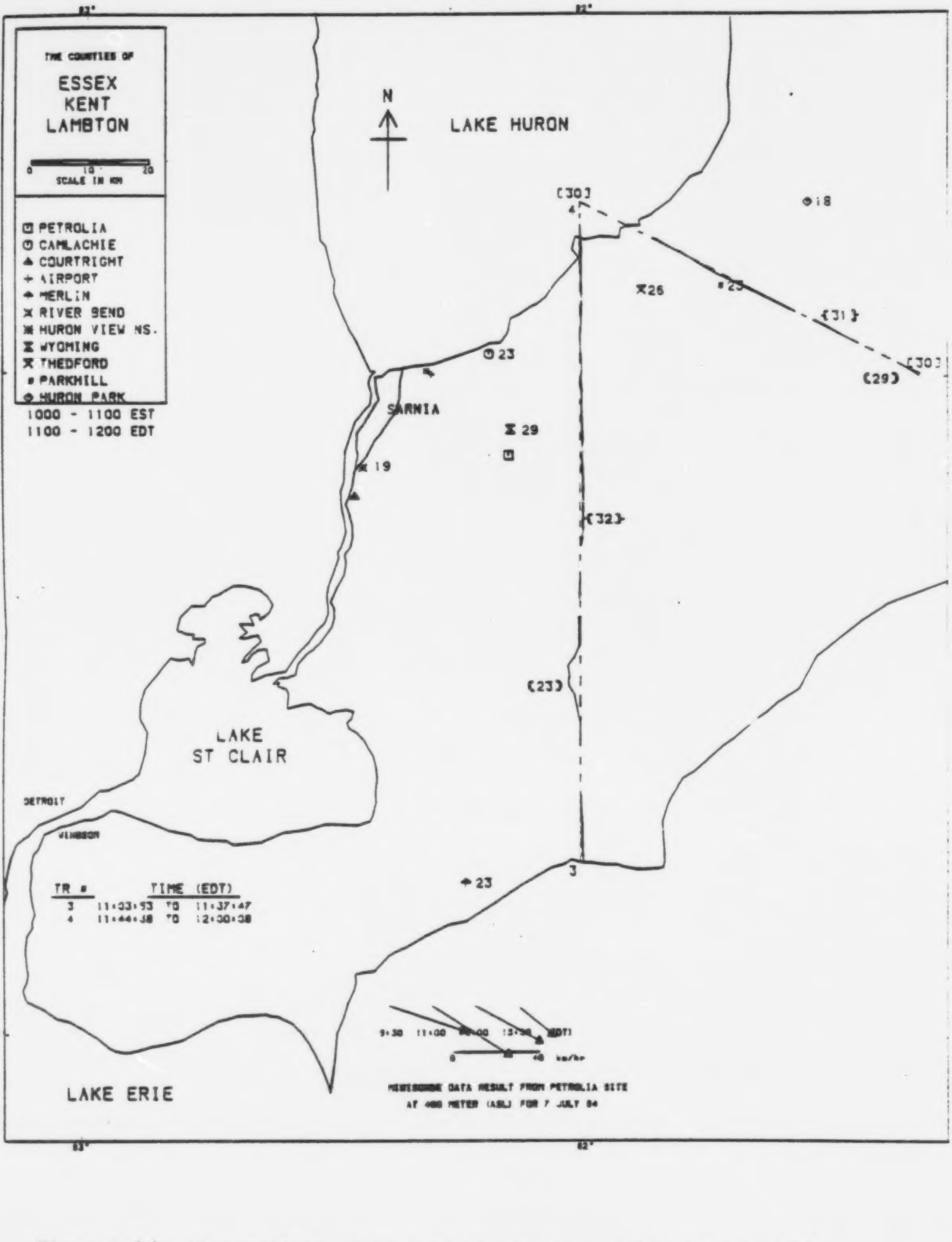

83°
82°
THE COUNTIES OF
ESSEX
KENT
LAMBTON
0 10 20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
1000 - 1100 EST
1100 - 1200 EDT
N
LAKE HURON
[30]
4
18
26
23
{31}
[30]
{29}
43°
23
SARNIA
29
19
{32}
{23}
LAKE
ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
3 11:33:53 TO 11:37:47
4 11:44:38 TO 12:30:38
23
3
9:30 11:00 12:00 13:30 (EDT)
0 40 km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 400 METER (ASL) FOR 7 JULY 84
42°
LAKE ERIE
83°
82°

Figure 18(b): Ozone Observations in the Sarnia Area on July 7, 11-12 EDT

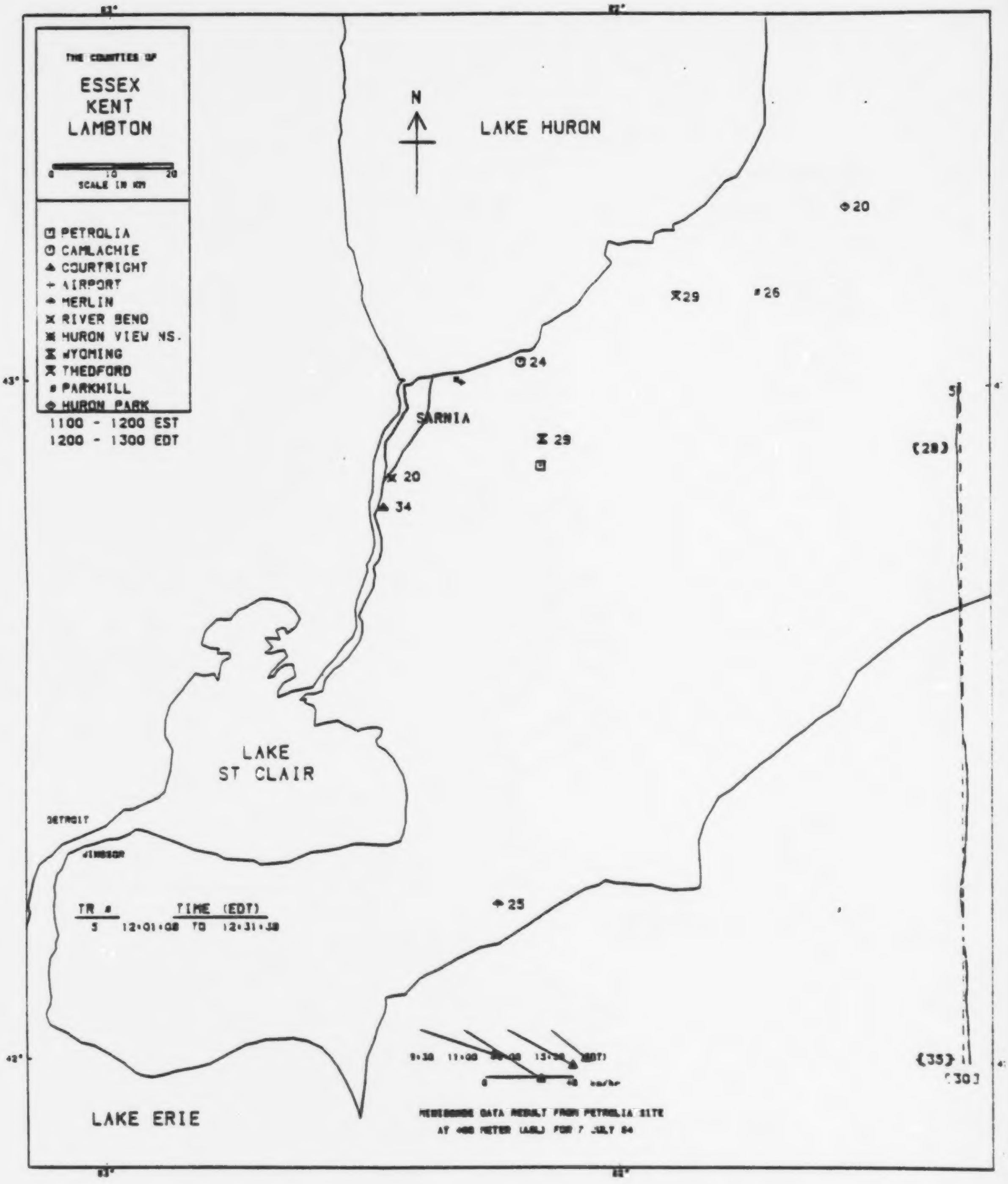

83°
82°
43°
42°
THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
1100 - 1200 EST
1200 - 1300 EDT
N
LAKE HURON
20
29
26
24
SARNIA
29
20
34
(28)
LAKE
ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
5
12:01:08 TO 12:31:38
25
9:30
11:00
15:30
(EDT)
0
40
km/hr
DATA RESULT FROM PETROLIA SITE
METER (AGL) FOR 7 JULY 84
LAKE ERIE
(35)
(30)

Figure 18(c): Ozone Observations in the Sarnia Area on July 7, 12-13 EDT

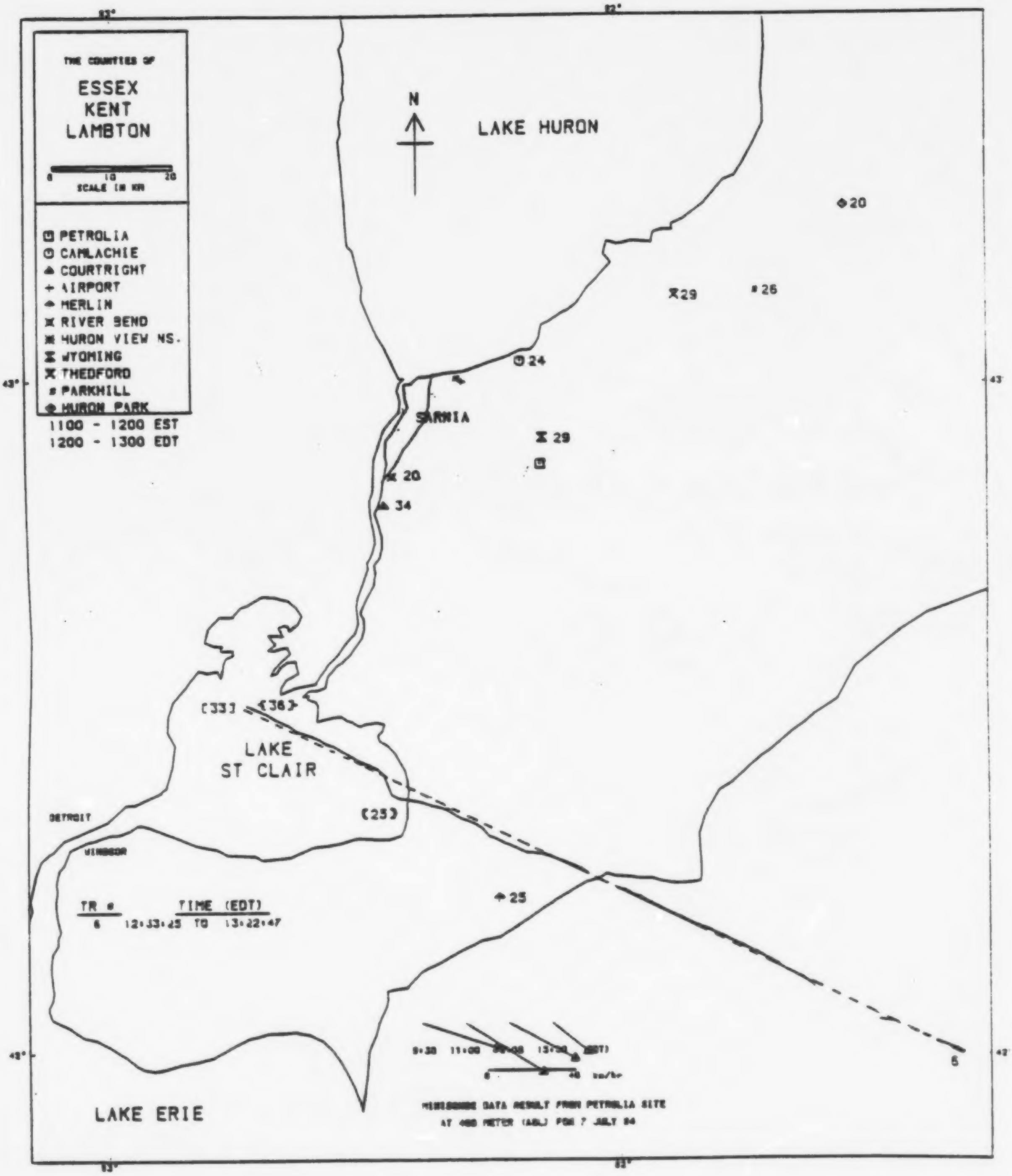

83°
82°
THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
1100 - 1200 EST
1200 - 1300 EDT
N
LAKE HURON
20
29
26
24
SARNIA
29
20
34
43°
[33]
[36]
LAKE
ST CLAIR
[25]
DETROIT
WINDSOR
25
TR #
6
TIME (EDT)
12:33:45 TO 13:22:47
9:30
11:00
13:30
(EDT)
0
40
km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 400 METER (AGL) FOR 7 JULY 84
5
42°
LAKE ERIE

Figure 18(d): Ozone Observations in the Sarnia Area on July 7, 12-13 EDT (continued)

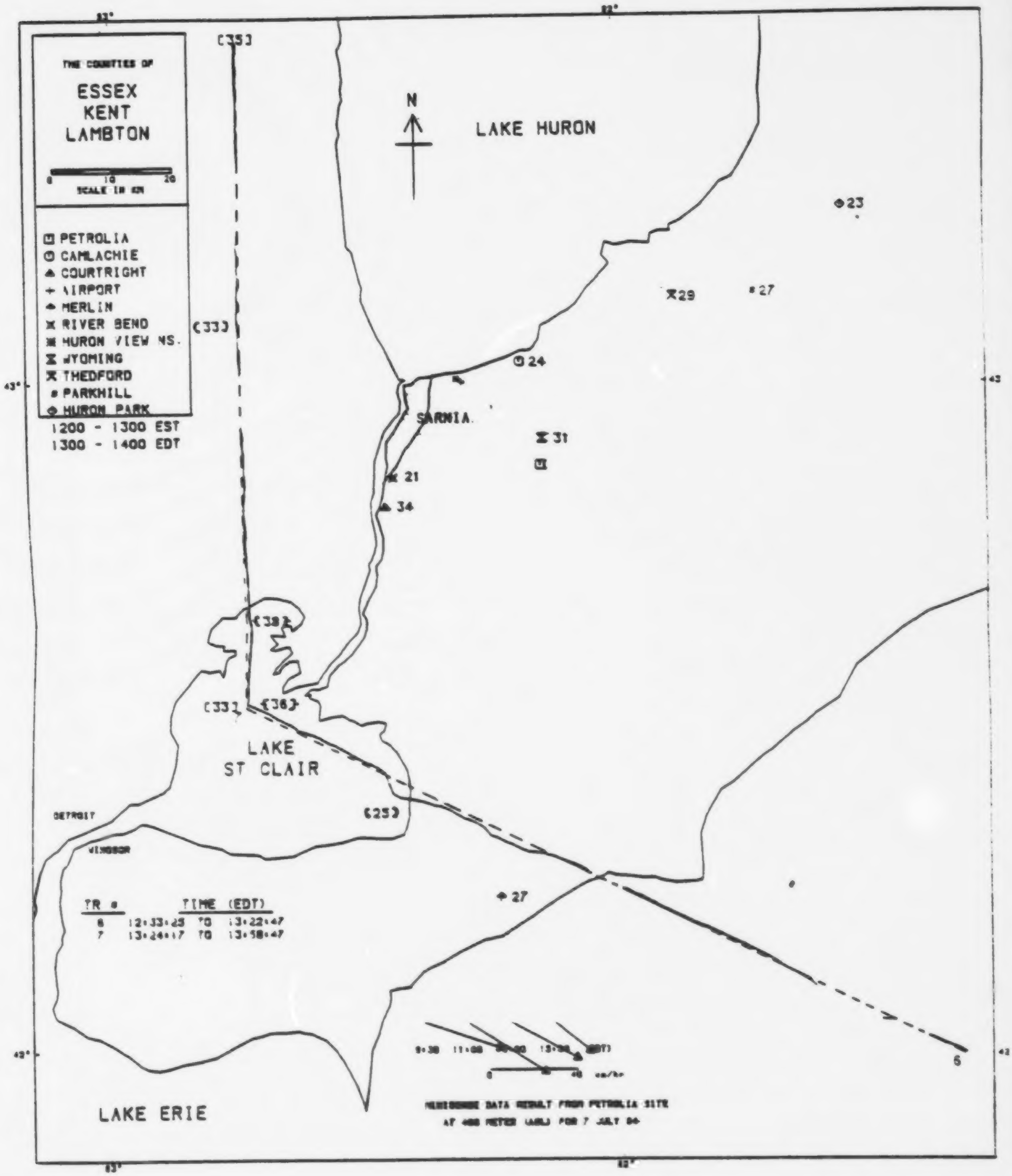

83°
82°
43°
42°
THE COUNTIES OF
ESSEX
KENT
LAMBTON
0 10 20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
1200 - 1300 EST
1300 - 1400 EDT
N
LAKE HURON
[35]
[33]
23
29
27
24
SARNIA
31
21
34
[38]
[33]
[36]
LAKE
ST CLAIR
DETROIT
WINDSOR
[25]
27
6
TR #
TIME (EDT)
6 12:33:25 TO 13:22:47
7 13:24:17 TO 13:58:47
9:30 11:00 13:30 (EDT)
0 40 km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 400 METER (AGL) FOR 7 JULY 84
LAKE ERIE

Figure 18(e): Ozone Observations in the Sarnia Area on July 7, 13-14 EDT

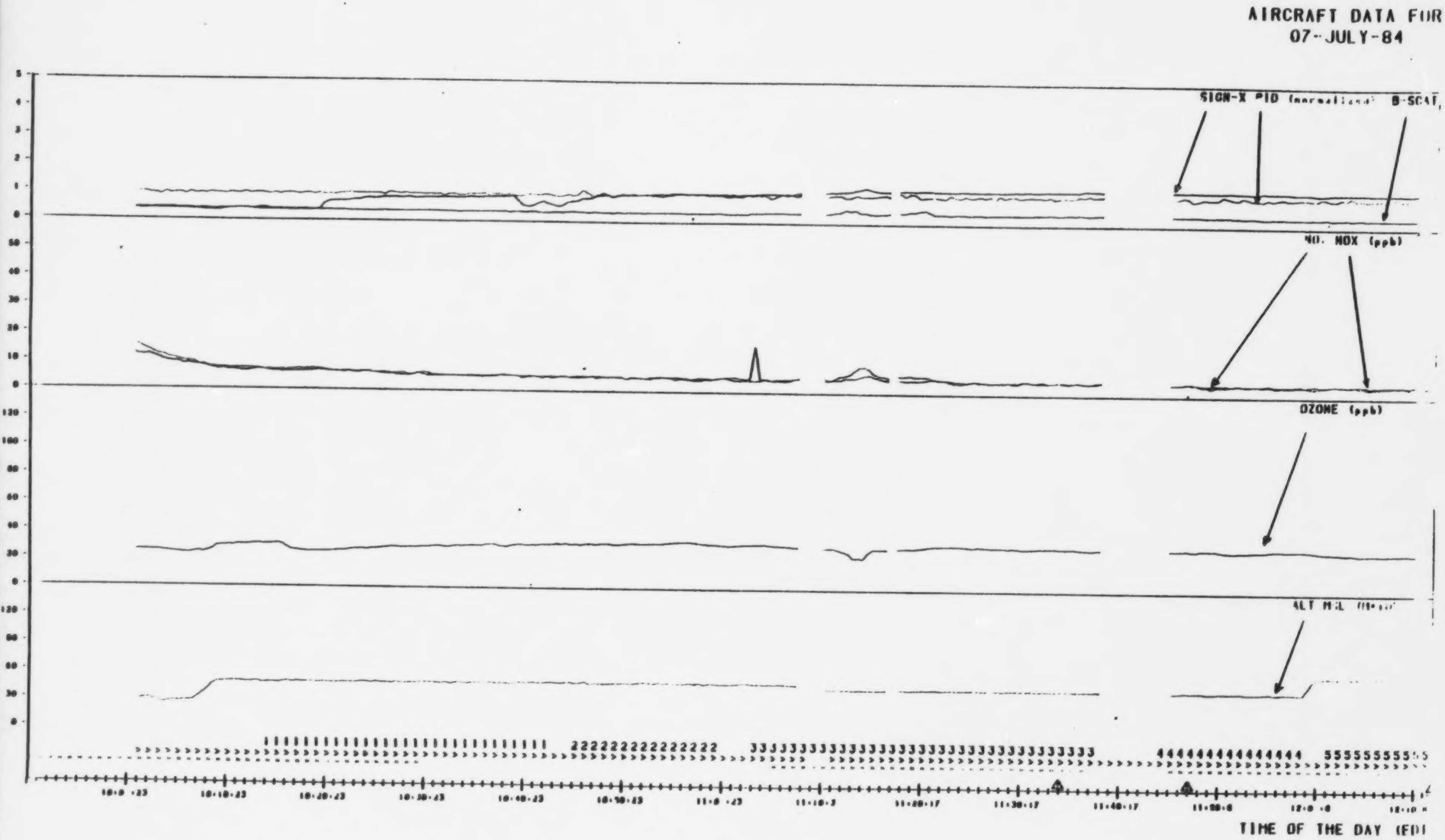


Figure 19: Aircraft Observations on July 7

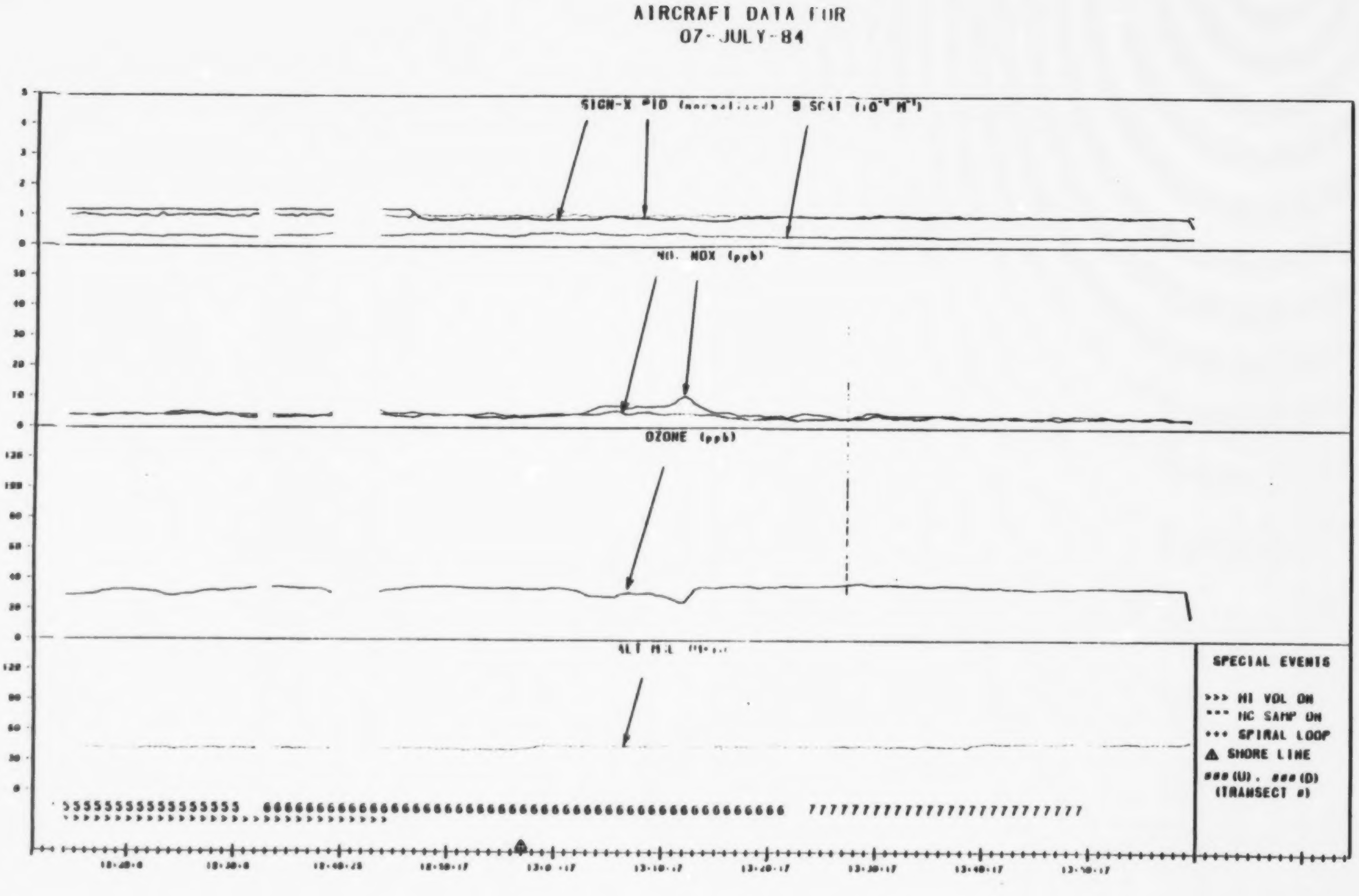


Figure 19: Aircraft Observations on July 7 (continued)

3.6 July 8

On July 8, a quasi-stationary high pressure cell was centered over Ohio. As a result, the Sarnia region remained in a light and variable flow, with a weak lake breeze developing in the afternoon. In the early morning, a dome of brown haze (probably largely due to NO_2) was observed over the chemical valley area of Sarnia. For the period 0800-1800 EDT, winds were generally variable over the region in the morning, with speeds in the 5 to 10 km h^{-1} range, and variable to southeast (5 to 15 km h^{-1}) later in the afternoon. Mainly sunny skies prevailed, with afternoon temperatures in the low to mid-twenties. The daytime relative humidity was in the 40-50% range at Courtright and Camlachie, with a maximum hourly average solar radiation of about 100 milliwatts per cm^{-2}. For the above period, the initial mixing height at 0800 EDT was about 150 m. The mixed layer grew to about 800 m by early afternoon, and fluctuated between 300-800 m during the afternoon. Near the end of the period, a stable ground layer developed.

Backward trajectories of air parcels (48 hours) over the Sarnia area during the study period indicate an air path southward through western Lake Superior and then southeastward across central Lake Michigan and into the Sarnia region. Ozone levels in the area were relatively low, with hourly averages at the ground level monitors generally below 40 ppb in the morning, and peaking to 60-70 ppb at some stations in the afternoon (Figure 20). Upwind sulfate and nitrate levels, as measured by the aircraft's high volume filter pack, were relatively low at 6.0 and 2.2 ug m^{-3} respectively, and nephelometer measurements also indicated the presence of fairly clean air in the study area, with readings generally at or below 0.5×10^{-4} m^{-1} (Figure 22(a)).

For the study period, forward air parcel trajectories show a general east-northeast movement, but due to the light and variable winds, it was not possible to clearly define upwind or downwind directions. Therefore, some of the traverses carried out on the two flights this day, which were originally thought to be downwind of Sarnia, may in fact not have been sampling Sarnia emissions.

The morning flight (0900-1200 EDT) started with a number of traverses (at about 200 m above ground) within roughly 20 km of Sarnia (traverses 1-5 Figures 21(a) to (c)). There was a considerable "patchiness" in the ozone levels aloft, with pockets having concentrations as high as 80 ppb in places and as low as 20 ppb elsewhere, and some evidence as well of NO_x plumes and high local levels of light-scattering particulates (Figure 22(a)). Two hydrocarbon samples collected during these flights suggested the presence of Sarnia emissions, because of the high levels of aromtics and alkanes (37-41, and 42-72 ug m^{-3} respectively). These observations are no doubt due to the light wind speeds and the atmospheric stratification at the time (before 1000 hours EDT). That the high local ozone levels aloft are due to local emissions, rather than being remnants of aged, polluted air parcels from elsewhere, is suggested by the light and variable winds at the time of measurement, and the fact that during the preceding day ozone levels across the study area were also low (Figure 17), i.e. the air mass was clean. Lusis et al. (1976) have found similar, apparently rapid buildups of early morning ozone levels from local emissions in stable air, in an aircraft study in the metropolitan Toronto area. The ground level measurements show fairly uniform regional concentrations, with some evidence of ozone scavenging by local nitrogen oxide emissions in the Sarnia area. In general, ozone values aloft seem to be higher than at ground level, and there is no clear evidence of any urban "plume" in the data from the morning flight. Nevertheless, the impact of Sarnia emissions on ozone concentrations in the area seems to manifest itself as local "patches" of high ozone levels within about 20 km of the industrial area.

The afternoon flight on July 8 (from about 1500 to 1830 EDT) is even more difficult to interpret, because the regional wind shift from the northwesterly to southeasterly direction occurred just before the start of the flight. Most of the aircraft sampling took place within about 40 km, and in all directions around Sarnia, since it was difficult under the circumstances to identify any "upwind" or "downwind" sample (Figures 21(f) to (i)). The flight was completed by two elliptical paths at 300 to 400 metres altitude over Sarnia.

Except for samples collected to the north-northwest of Sarnia, where ozone concentrations were fairly uniform, several broad areas of elevated ozone were observed in the Sarnia area, where ozone rose to maximum values in excess of 60 ppb (as compared to roughly 40 ppb measured elsewhere, as well as at the more distant ground level stations such as Thedford and Parkhill). These areas of elevated ozone were often associated with detectable increases in the concentations of light-scattering particulates and nitrogen dioxide - see Figure 22(b). The elliptical sampling path showed relatively higher (by about 15 ppb) ozone levels on the west than on the east side of the St. Clair river, but there was evidence of scavenging by elevated plumes, since concurrent local high (up to about 30 ppb) NO_x concentrations were observed. Because of the light and variable winds during the sampling period, it is difficult to attribute the observed areas of elevated ozone to Sarnia emissions, although this is strongly suspected to be the case. It is interesting to observe that both the ground level, and the aircraft ozone measurements suggest relatively high levels outside the Sarnia area, tapering off to regional levels of about 40-45 ppb farther afield (except possibly over the lake, where slightly higher values are indicated). Within Sarnia, ozone levels are relatively low (as expected, due to scavenging by local NO emissions). Three hydrocarbon samples were collected during this flight: the first two were lower in hydrocarbon concentration than the morning samples (37-47 ug m^{-3}), although the levels of aromatics were similar (31 and 32 ug m^{-3}). The third sample, collected during the elliptical flight over Sarnia, had relatively high non-methane hydrocarbon, alkane, alkene and aromatic levels (81, 49, 0.8 and 29 ug m^{-3}respectively).

Some other measurement results on this day are of interest:

(i) An examination of the hydrocarbon and nitrogen oxide data at the continuous sites within Sarnia suggested a buildup of these species in the early morning, as hourly average concentations tended to be higher than the corresponding monthly means for the same hours (though not at all sites). This would be as expected, due to the relatively calm conditions, and was confirmed by the observed presence of the brown pollution dome over the industrial area. The hydrocarbon samples collected between 8-10 hours EDT, both in the aircraft over Sarnia, and at Courtright and

Camlachie (where relatively high levels were detected), are therefore of particular interest, since they should give a "signature" for the overall composition of emissions from the Sarnia area. The table below summarizes these results, and also includes the results of the afternoon aircraft flight over Sarnia.

Location	Time (EDT)	Total HC (C_{3+})ug m^{-3}	Alkanes %	Alkenes %	Aromatics % (benzene)
Camlachie	0818-0916	140	84	0.8	11 (5)
Courtright	0909-1009	47	79	0.3	13 (3)
Airplane	0918-0948	88	50	0.6	47 (12)
	0950-1020	113	65	0.8	33 (7)
	1802-1817	81	63	0.9	36 (5)

Note that all the above samples indicate very low concentrations (less than 1% by weight) of the photochemically reactive alkenes in the Sarnia emissions. The relatively unreactive alkanes and benzene (shown in brackets in the above table) make up a large portion of the ambient hydrocarbons. The composition of the aircraft and ground level samples seems to be different, the latter having a larger percentage (more than 50%) contribution from propane, butane, methylbutane and pentane, while the former have much lower, or undetectable, levels of these compounds. On the other hand, the aircraft samples have appreciable amounts of the relatively reactive alkyl-benzenes. The low reactivity (with respect to ozone formation) of the hydrocarbon / NO_x mixture measured at the Courtright and Camlachie sites in the morning is confirmed by the ozone precursor monitor results, which gave very low values (about 4-5 ppb ozone) at both locations. It is interesting to speculate that the pockets of elevated ozone levels detected by the aircraft in the Sarnia area on this day may have been generated by the apparently higher concentrations of the reactive alkyl benzenes aloft (possibly from elevated sources). This hypothesis is supported by the fact that there were observable increases in the continuous photoionization hydrocarbon analyser readings generally concurrent with increases in ozone levels (Figure 22(a)), but there are two provisos which must be kept in mind: (1) both in the aircraft and at the ground monitoring sites, NO_x levels were generally near or below the instrument detection limits (except when plumes were being traversed by the aircraft), so we have little information on NO_x concentrations in the aircraft as compared to Courtright or Camlachie; and (2) there is a possibility that the aircraft hydrocarbon samples may have had elevated alkyl benzene concentrations due to contamination (see the discussion under the July 3 and 7 flights).

(ii) Measurements were made of various aldehydes, ketones, acetates and alcohols at Courtright, and of formaldehyde at Camlachie. The aldehyde levels at Courtright (propanal, butanal, pentanal) increased slightly through the day from 0.3 - 0.9 pbb before 0900 hours to 0.5 - 1.5 ppb at about 1500 hours. Formaldehyde was monitored at Camlachie in the late afternoon, and found to be at relatively high concentrations (4 - 5 ppb). Ketones and acetates at Courtright were low throughout the day (less than 0.5 ppb), while alcohols (methanol - butanol) were in the 1-5 ppb range, and showed no clear diurnal variation.

To summarize the observations on this day: winds were light and variable, and there was considerable structure in the ozone concentrations in the area, with aircraft data indicating pockets of high ozone concentrations suspected to be due to Sarnia emissions (possibly from elevated emission sources of alkyl benzenes). The afternoon ground level data also showed elevated ozone concentrations at the Courtright, Camlachie and Wyoming stations, possibly attributable to Sarnia. While the early morning hydrocarbon measurements at all sample collection sites were high, and no doubt had a significant component due to Sarnia industries, the ozone precursor monitor indicated that the ozone forming potential of the mixture was low, probably because the majority of the hydrocarbons consisted of the relatively unreactive alkanes and benzene.

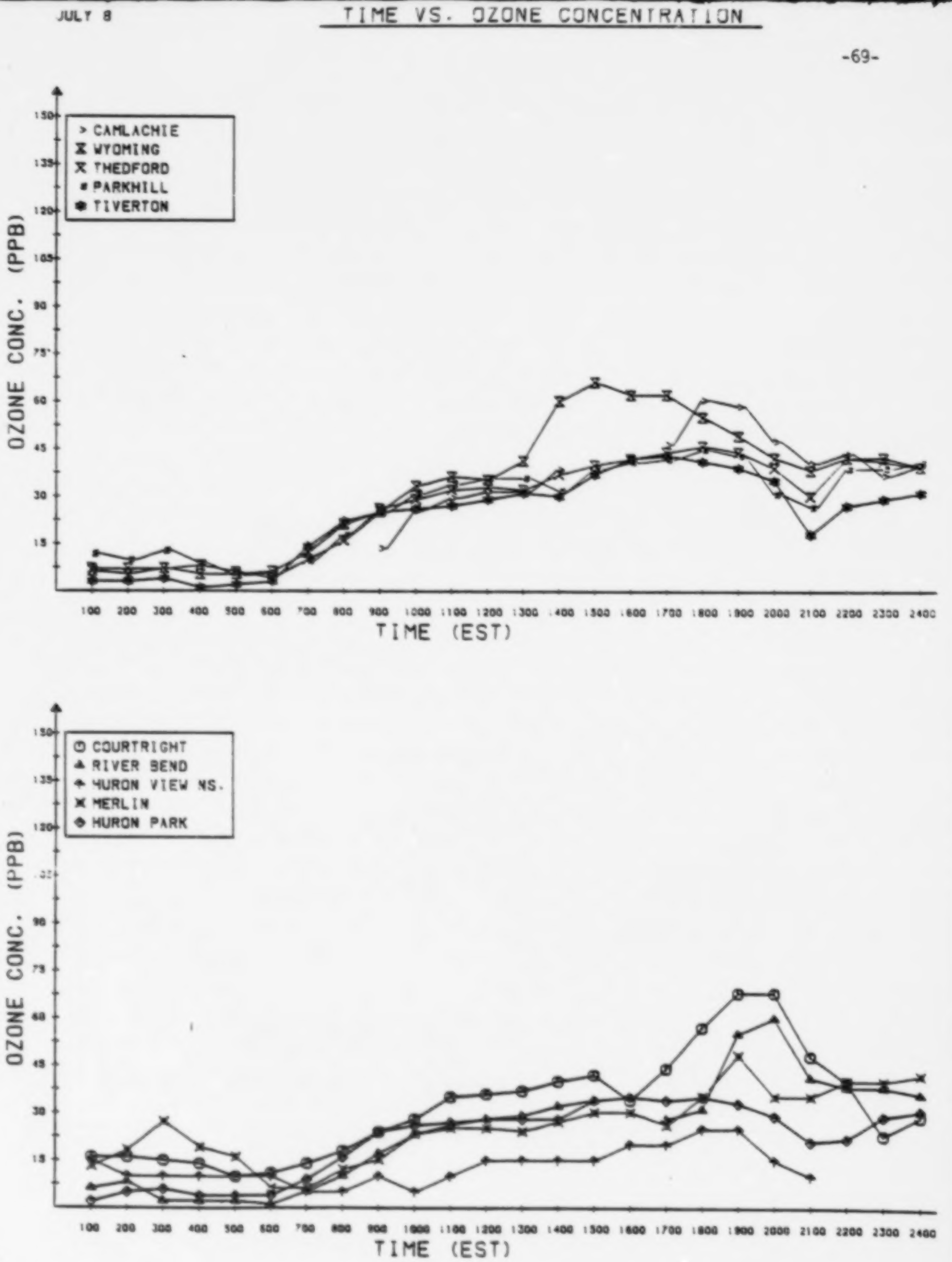


Figure 20: Diurnal Variation of Ozone Concentrations in the Sarnia Area, July 8

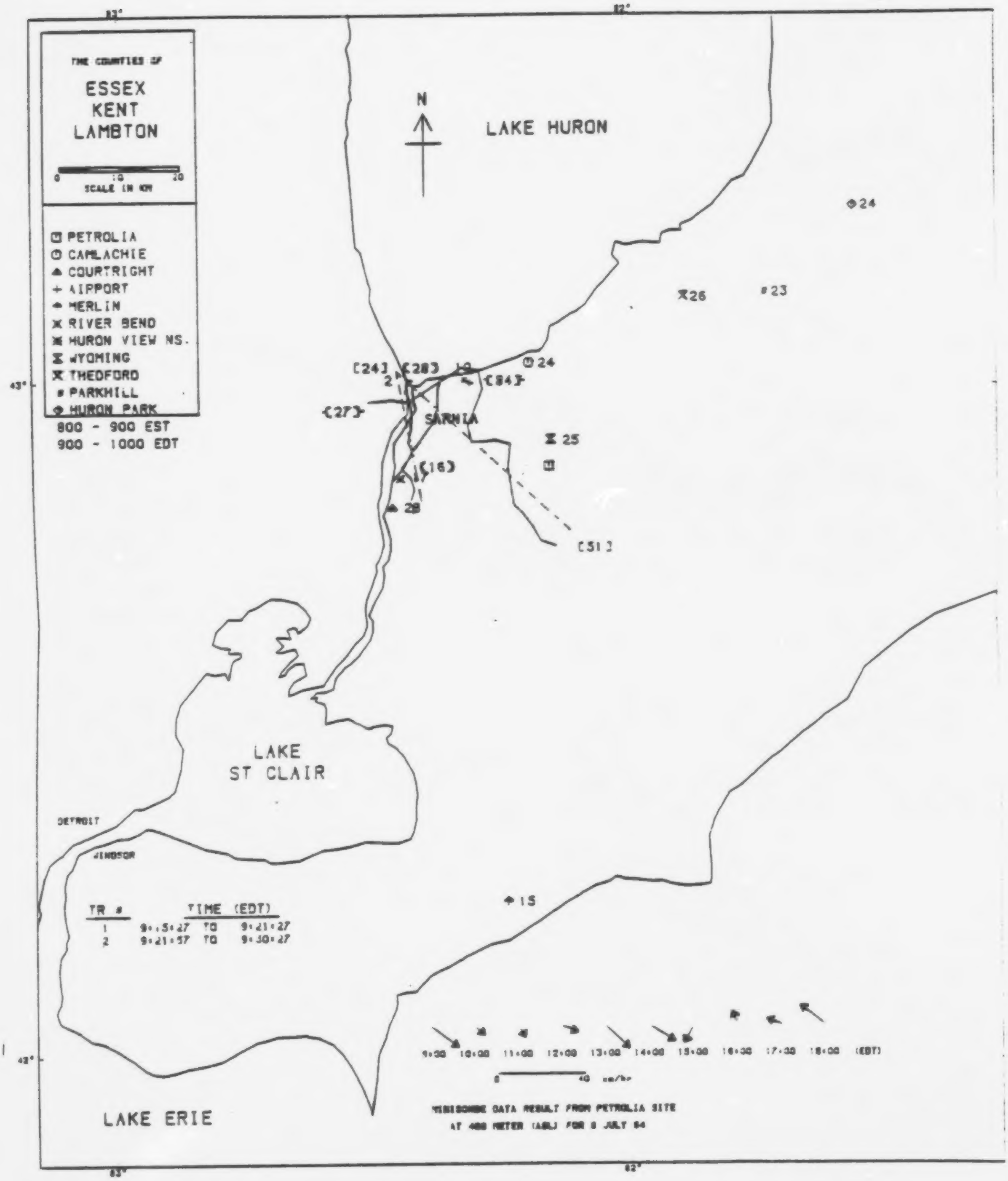

83°
82°
THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIPPORT
MERLIN
RIVER BEND
HURON VIEW NS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
800 - 900 EST
900 - 1000 EDT
N
LAKE HURON
24
26
23
[24]
[28]
2
10
24
[84]
[27]
SARNIA
25
[16]
28
[51]
43°
42°
LAKE
ST CLAIR
DETROIT
WINDSOR
15
TR #
TIME (EDT)
1
9:15:27 TO 9:21:27
2
9:21:57 TO 9:30:27
9:30
10:00
11:00
12:00
13:00
14:00
15:00
16:30
17:30
18:00
(EDT)
0
40
km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 400 METER (AGL) FOR 8 JULY 84
LAKE ERIE

Figure 21(a): Ozone Observations in the Sarnia Area on July 8, 9-10 EDT

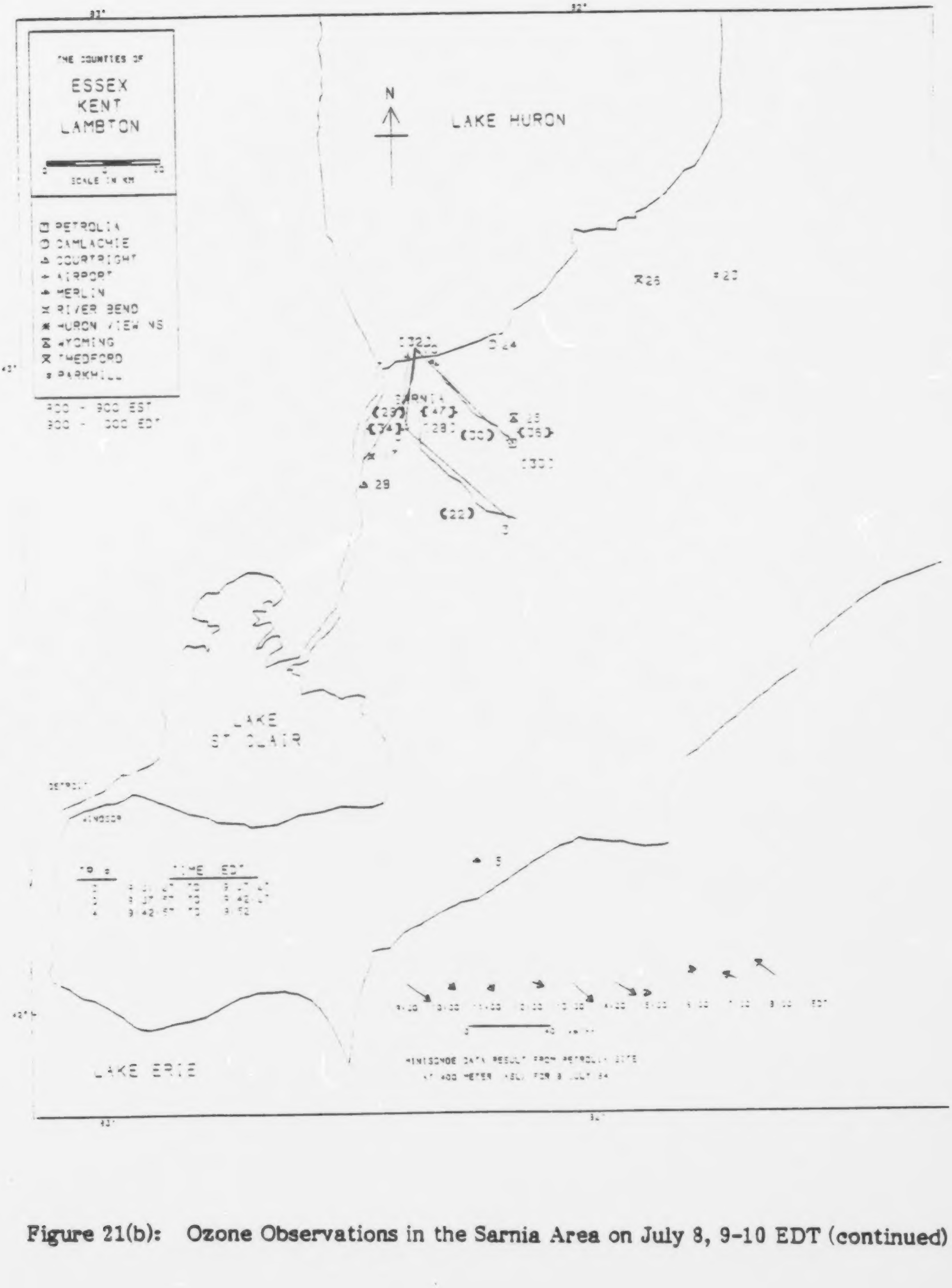

THE COUNTIES OF
ESSEX
KENT
LAMBTON
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS
WYOMING
THEDFORD
PARKHILL
800 - 900 EST
900 - 1000 EDT
N
LAKE HURON
SARNIA
24
26
20
47
28
29
22
LAKE ST CLAIR
DETROIT
WINDSOR
TIME EDT
9:42:57 TO 9:52
5
EDT
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 400 METER (ASL) FOR 8 JULY 84
LAKE ERIE

Figure 21(b): Ozone Observations in the Sarnia Area on July 8, 9-10 EDT (continued)

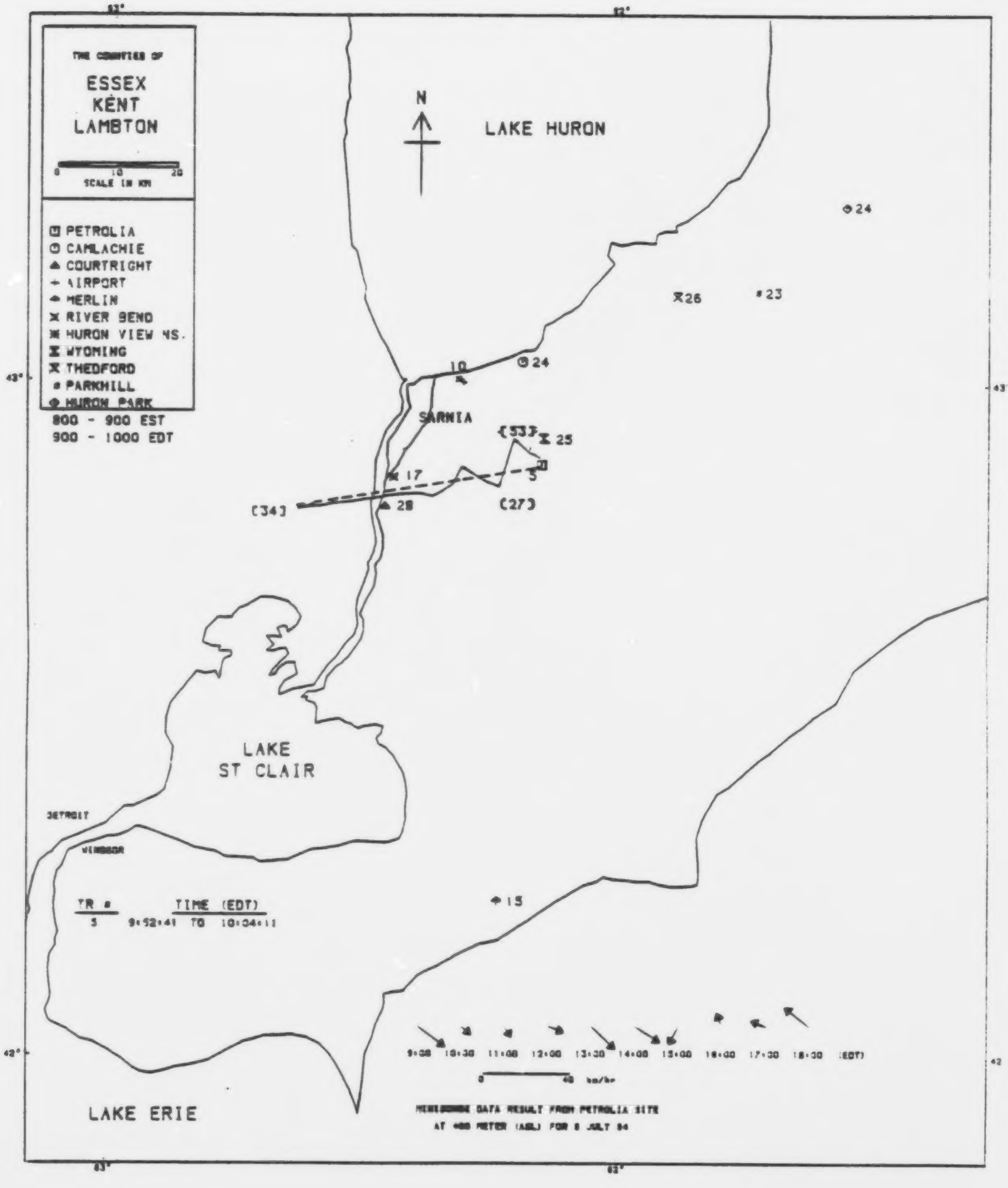

83°
82°
43°
42°
THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW HS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
800 - 900 EST
900 - 1000 EDT
N
LAKE HURON
24
26
23
10
24
SARNIA
{53}
25
17
5
[34]
28
[27]
LAKE ST CLAIR
DETROIT
WINDSOR
TR #
5
TIME (EDT)
9:52:41 TO 10:04:11
15
LAKE ERIE
9:30
10:30
11:00
12:00
13:30
14:00
15:00
16:00
17:30
18:30
(EDT)
0
40 km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 400 METER (ASL) FOR 8 JULY 84

Figure 21(c): Ozone Observations in the Sarnia Area on July 8, 9-10 EDT (continued)

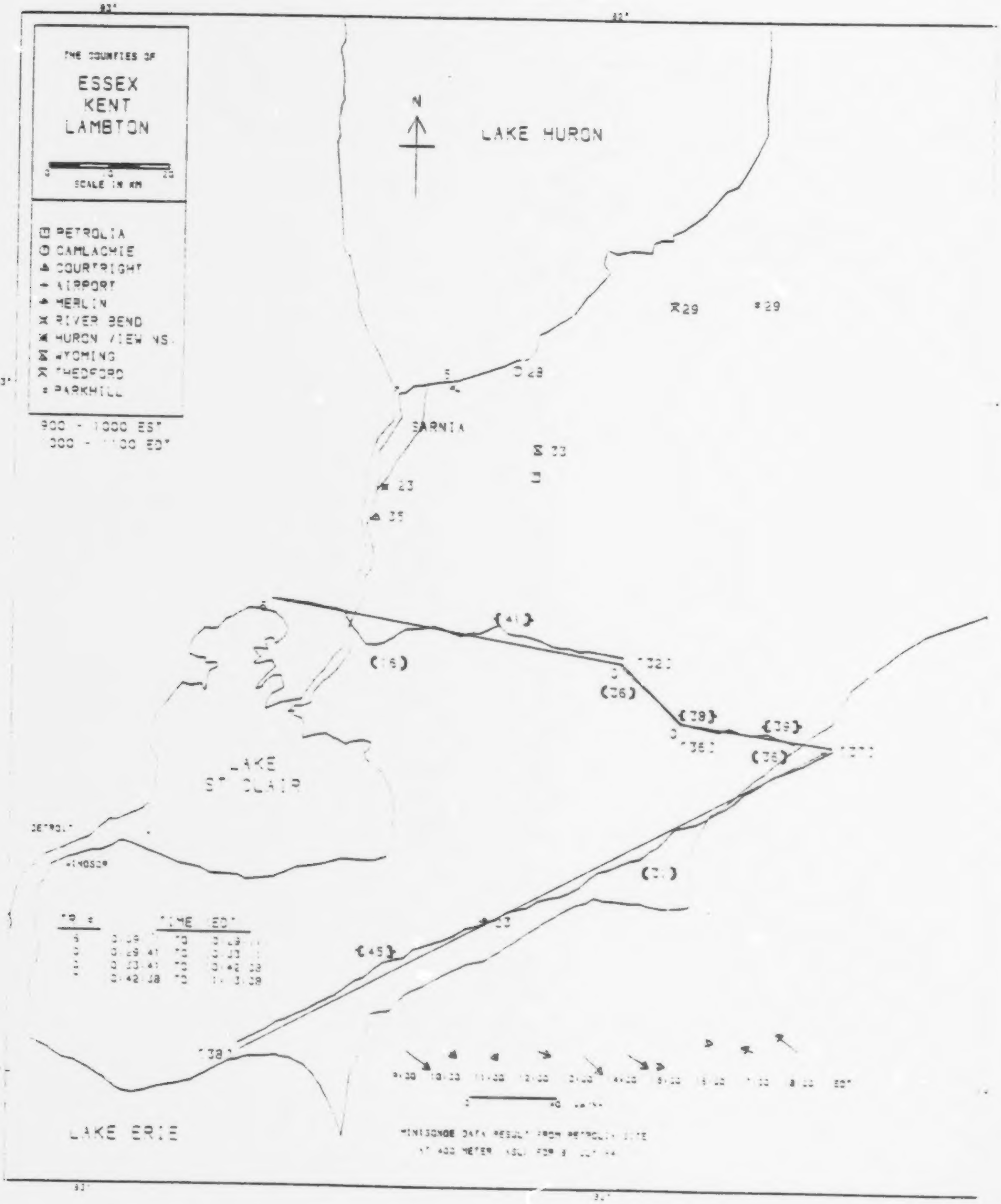

THE COUNTIES OF
ESSEX
KENT
LAMBTON
SCALE IN KM
0
10
20
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS.
WYOMING
THEDFORD
PARKHILL
900 - 1000 EST
1000 - 1100 EDT
N
LAKE HURON
29
29
28
SARNIA
23
23
35
LAKE ST CLAIR
DETROIT
WINDSOR
LAKE ERIE
41
16
32
36
39
39
36
45
38
23
9:00
10:00
11:00
12:00
EDT
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 400 METER ASL FOR 8 JULY 84
43°
42°

Figure 21(d): Ozone Observations in the Sarnia Area on July 8, 10-11 EDT

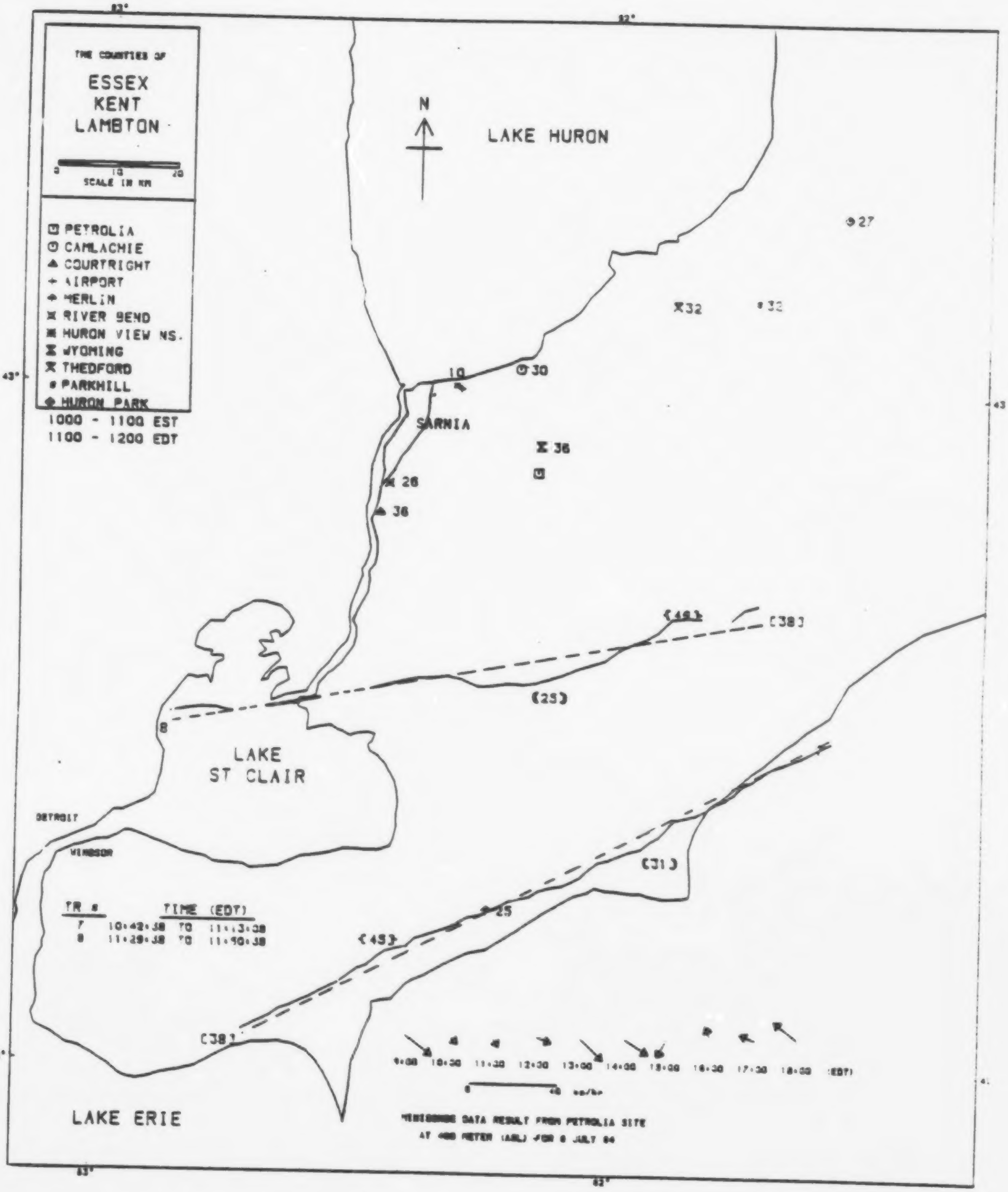

THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
20
SCALE IN KM
▣ PETROLIA
ⓞ CAMLACHIE
▲ COURTRIGHT
+ AIRPORT
✦ MERLIN
⌘ RIVER BEND
✱ HURON VIEW NS.
⧗ WYOMING
⧖ THEDFORD
• PARKHILL
◆ HURON PARK
1000 - 1100 EST
1100 - 1200 EDT
N
LAKE HURON
27
32
32
10
30
SARNIA
36
26
36
83°
82°
43°
{49}
[38]
(25)
8
LAKE
ST CLAIR
DETROIT
WINDSOR
[31]
25
{45}
[38]
TR #
TIME (EDT)
7 10:42:38 TO 11:13:38
8 11:29:38 TO 11:50:38
9:00
10:30
11:30
12:30
13:00
14:00
15:00
16:30
17:30
18:00
(EDT)
0
40 km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 400 METER (ASL) FOR 8 JULY 84
LAKE ERIE
42°

Figure 21(e): Ozone Observations in the Sarnia Area on July 8, 11-12 EDT

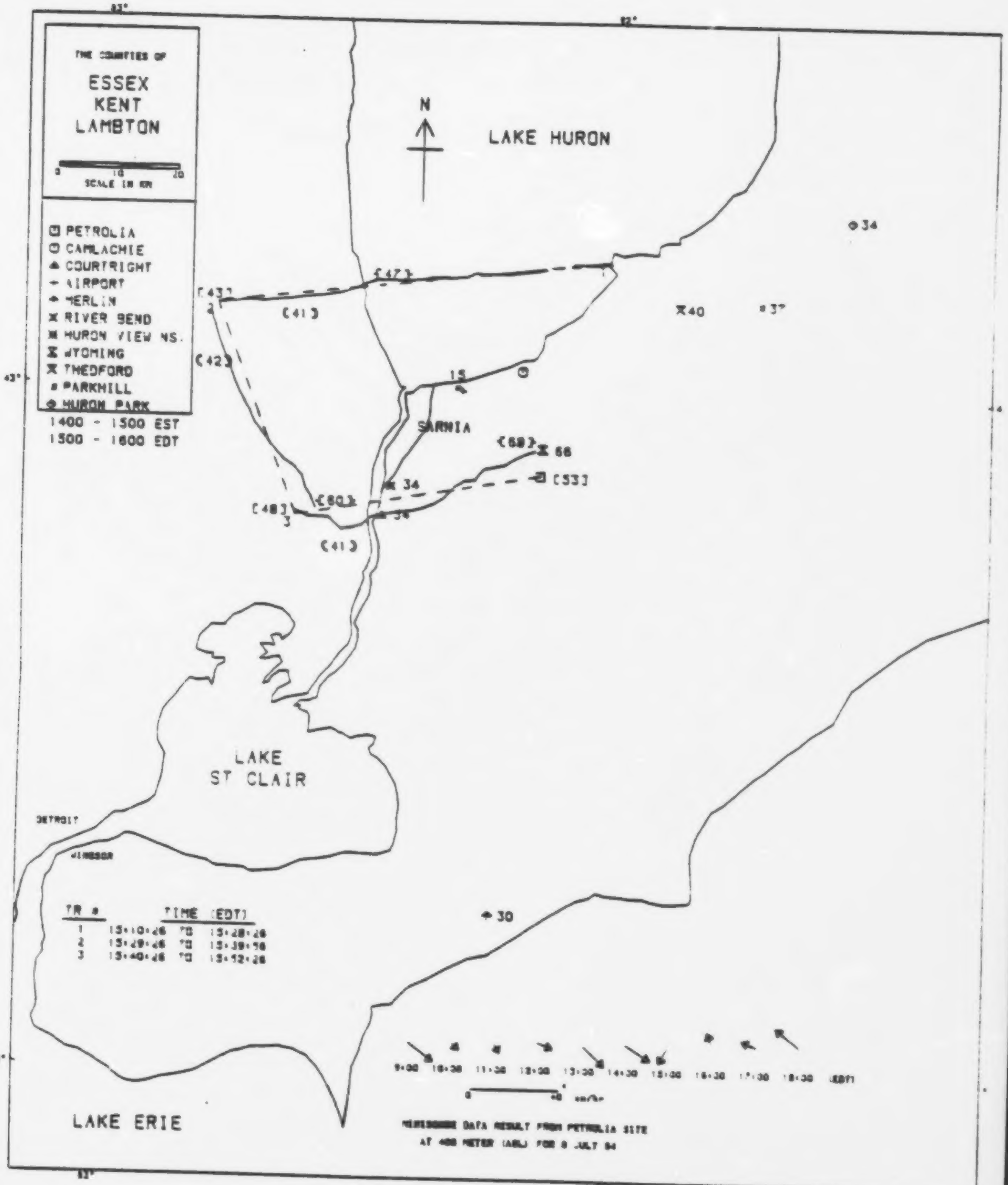

THE COUNTIES OF
ESSEX
KENT
LAMBTON
0 10 20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW HS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
1400 - 1500 EST
1500 - 1600 EDT
N
LAKE HURON
SARNIA
LAKE ST CLAIR
DETROIT
WINDSOR
LAKE ERIE
[47]
[43]
[41]
[42]
[68]
66
[53]
34
[60]
[48]
[41]
34
15
34
40
37
30
1
2
3
TR #
TIME (EDT)
1 15:10:26 TO 15:28:26
2 15:29:26 TO 15:39:56
3 15:40:26 TO 15:52:26
9:00 10:30 11:30 12:00 13:30 14:30 15:00 16:30 17:30 18:30 (EDT)
0 40 km/hr
MERISONDE DATA RESULT FROM PETROLIA SITE
AT 400 METER (AGL) FOR 8 JULY 94
42°
43°
82°
83°

Figure 21(f): Ozone Observations in the Sarnia Area on July 8, 15-16 EDT

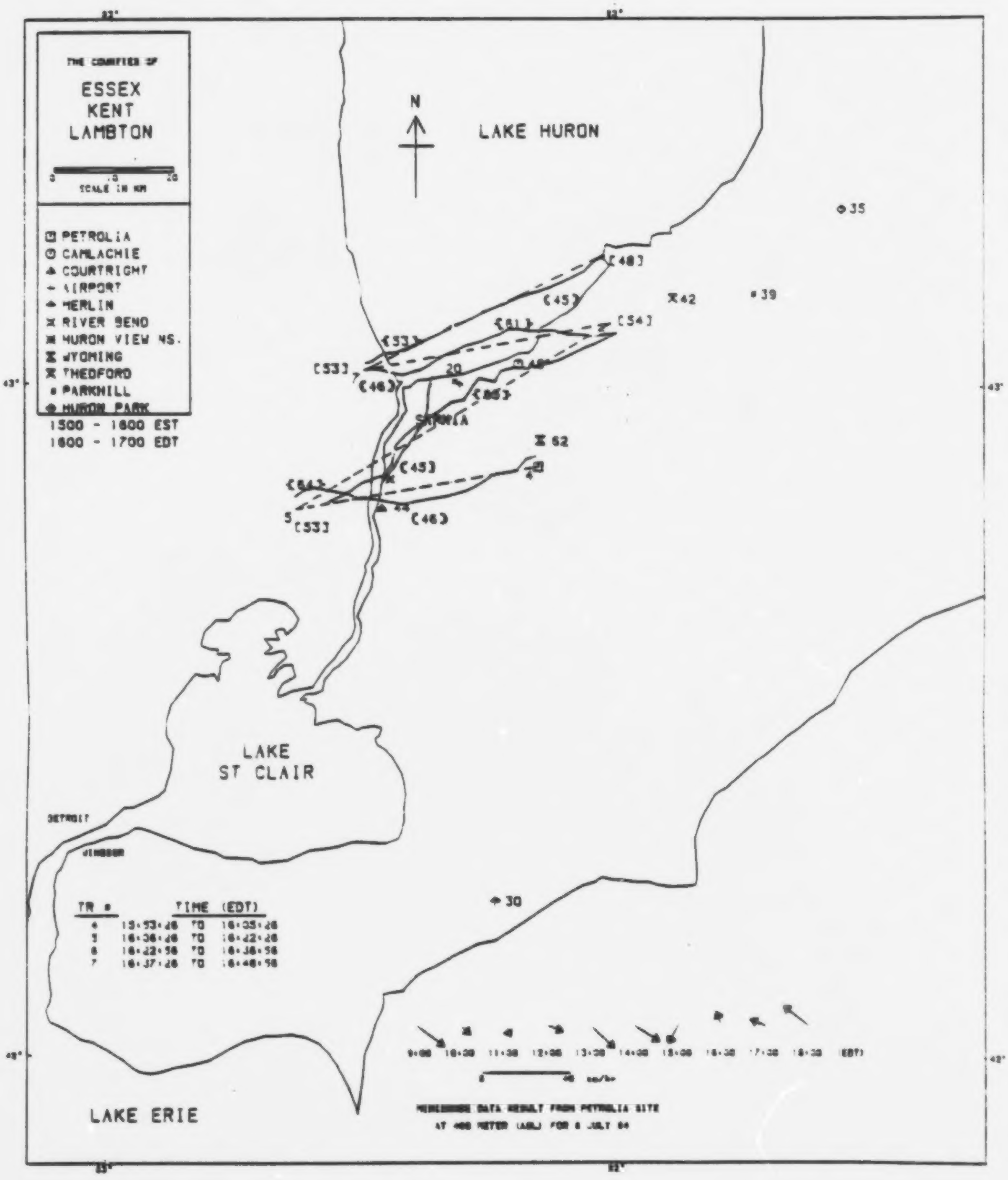

THE COUNTIES OF
ESSEX
KENT
LAMBTON
0 10 20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW HS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
1500 - 1600 EST
1600 - 1700 EDT
N
LAKE HURON
35
[48]
{45}
42
39
{81}
[54]
{53}
[53]
7
{46}
20
48
{86}
SARNIA
62
{45}
4
{64}
5
[53]
44
{46}
LAKE ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
4 15:53:26 TO 16:35:26
5 16:36:26 TO 16:42:26
6 16:22:56 TO 16:36:56
7 16:37:26 TO 16:48:56
30
9:00 10:00 11:00 12:00 13:00 14:00 15:00 16:00 17:00 18:00 (EDT)
0 40 km/hr
MESOSONDE DATA RESULT FROM PETROLIA SITE
AT 400 METER (AGL) FOR 8 JULY 84
LAKE ERIE
83°
82°
43°
42°

Figure 21(g): Ozone Observations in the Sarnia Area on July 8, 16-17 EDT

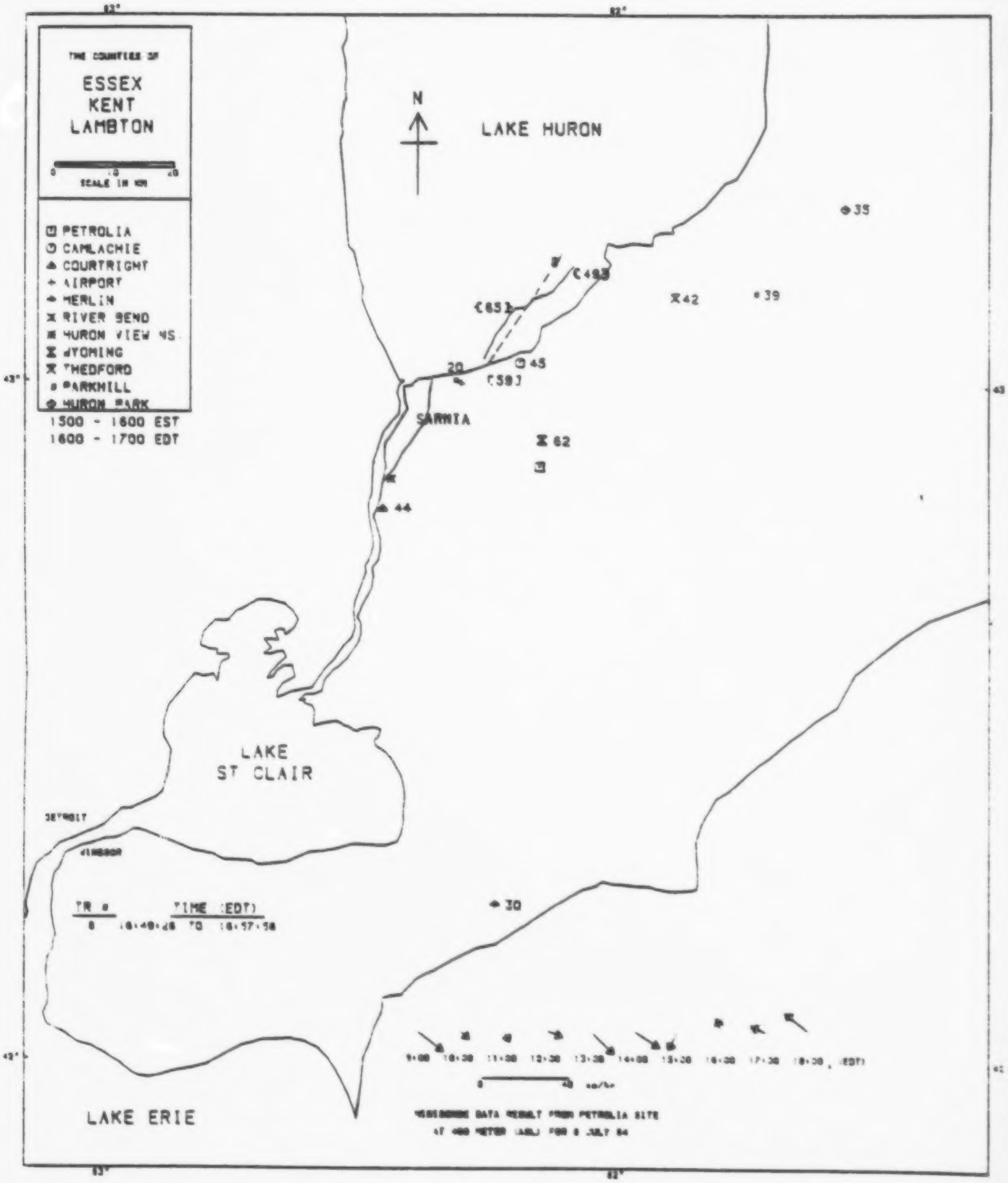

83°
82°
THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
40
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW HS
WYOMING
THEDFORD
PARKHILL
HURON PARK
1500 - 1600 EST
1600 - 1700 EDT
N
LAKE HURON
35
(49)
42
39
(63)
20
45
(59)
SARNIA
62
44
43°
LAKE
ST CLAIR
DETROIT
WINDSOR
TR #
8
TIME (EDT)
16:49:26 TO 16:57:56
30
9:00
10:30
11:30
12:30
13:30
14:00
15:30
16:30
17:30
18:30
(EDT)
0
40
km/hr
DATA RESULT FROM PETROLIA SITE
METER (AGL) FOR 8 JULY 84
42°
LAKE ERIE

Figure 21(h): Ozone Observations in the Sarnia Area on July 8, 16-17 EDT (continued)

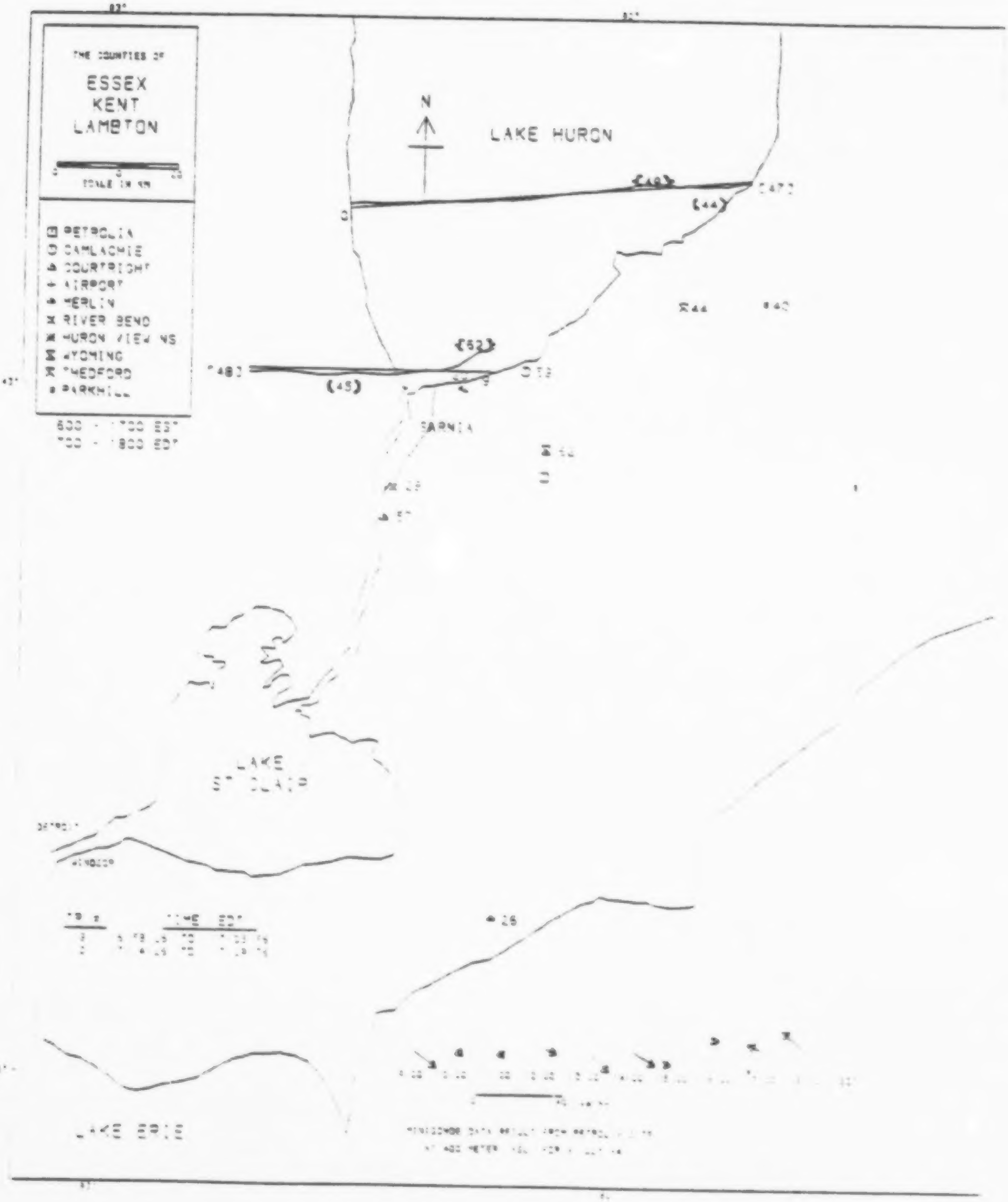

THE COUNTIES OF
ESSEX
KENT
LAMBTON
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS
WYOMING
THEDFORD
PARKHILL
600 - 1700 EST
700 - 1800 EDT
N
LAKE HURON
(49)
(44)
47
44
40
(52)
48
(45)
SARNIA
LAKE
ST CLAIR
DETROIT
WINDSOR
26
LAKE ERIE

Figure 21(i): Ozone Observations in the Sarnia Area on July 9, 17-18 EDT

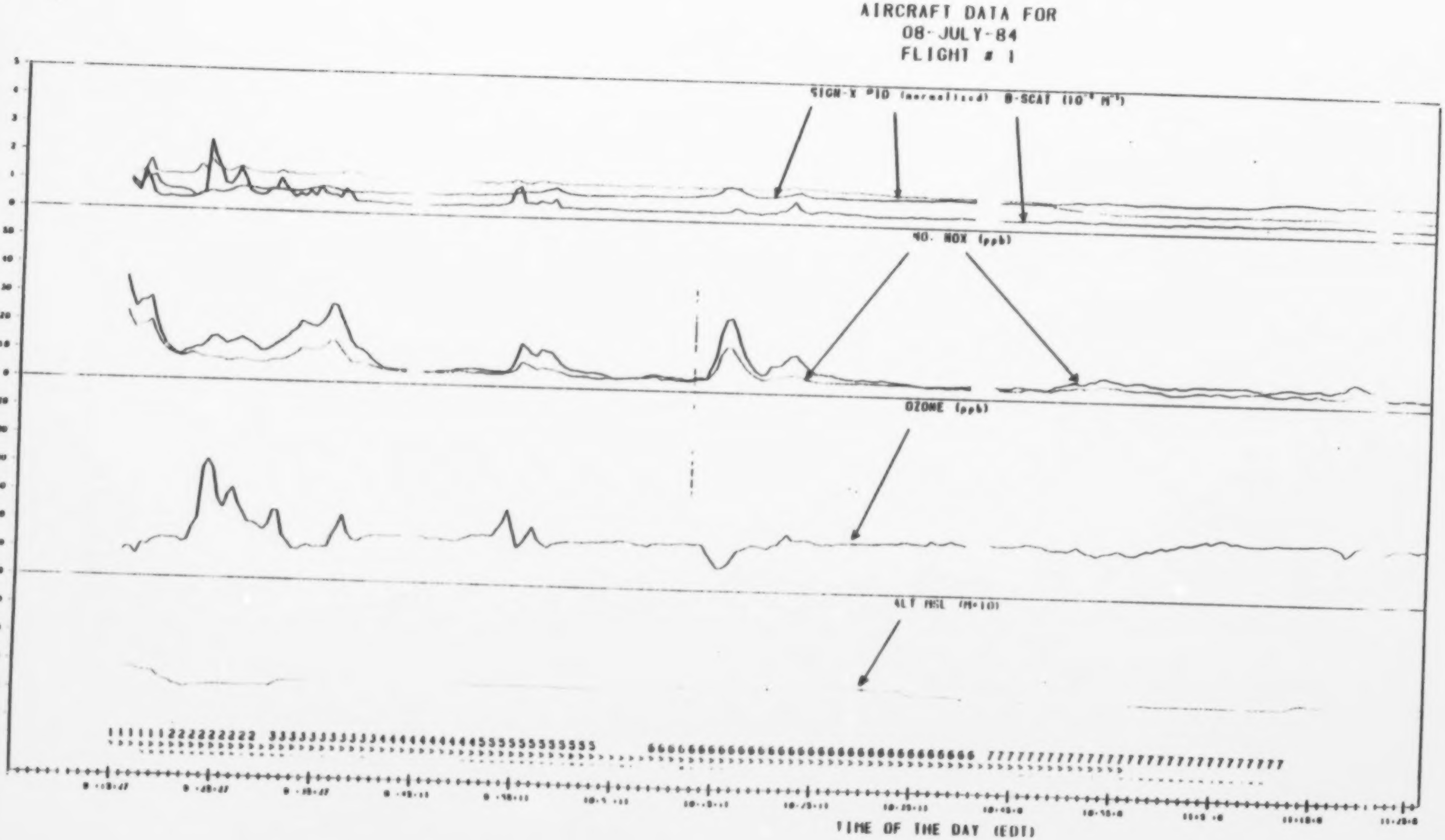


Figure 22(a): Aircraft Observations on July 8, 9-12 EDT

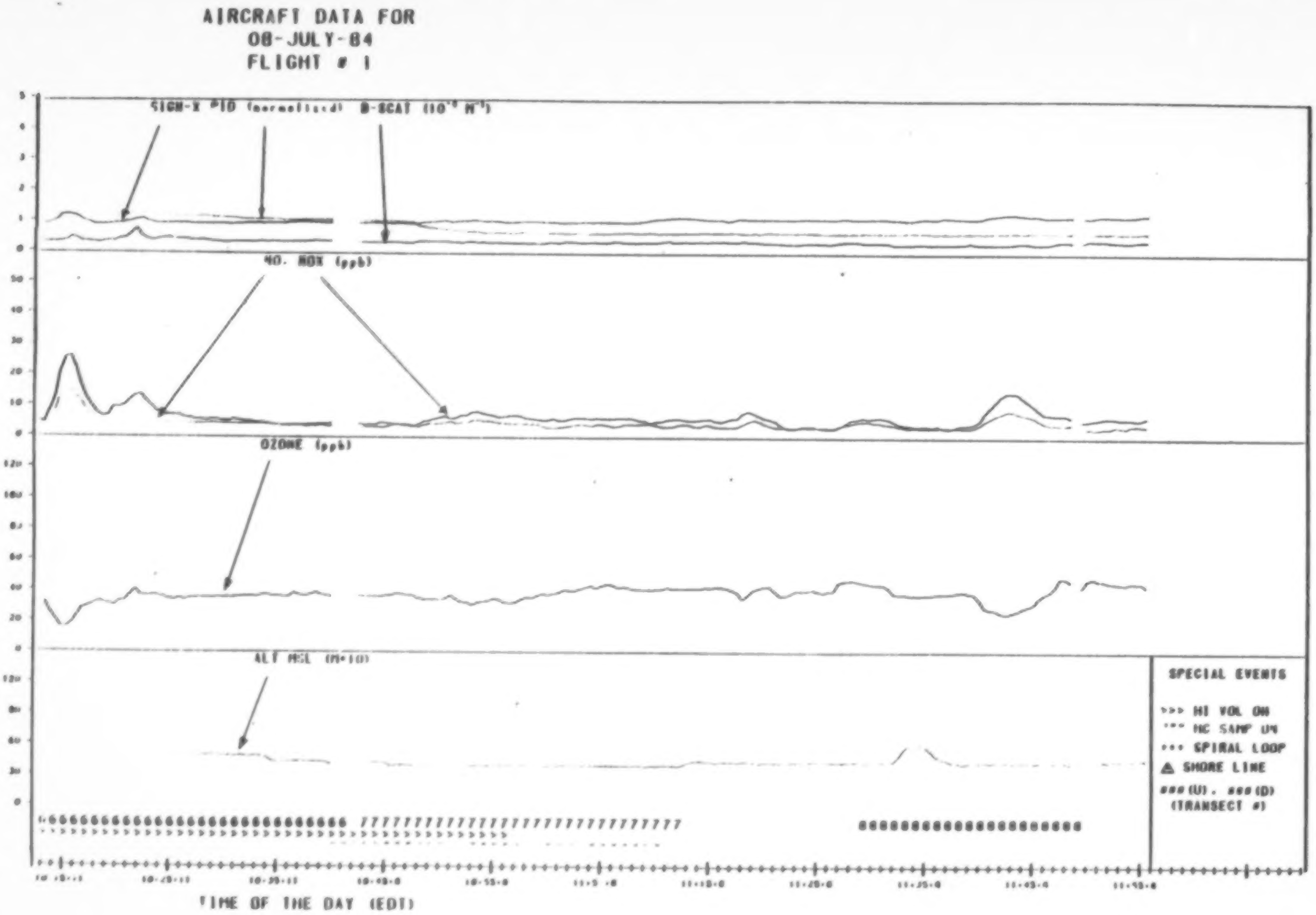


Figure 22(a): Aircraft Observations on July 8, 9-12 EDT (continued)

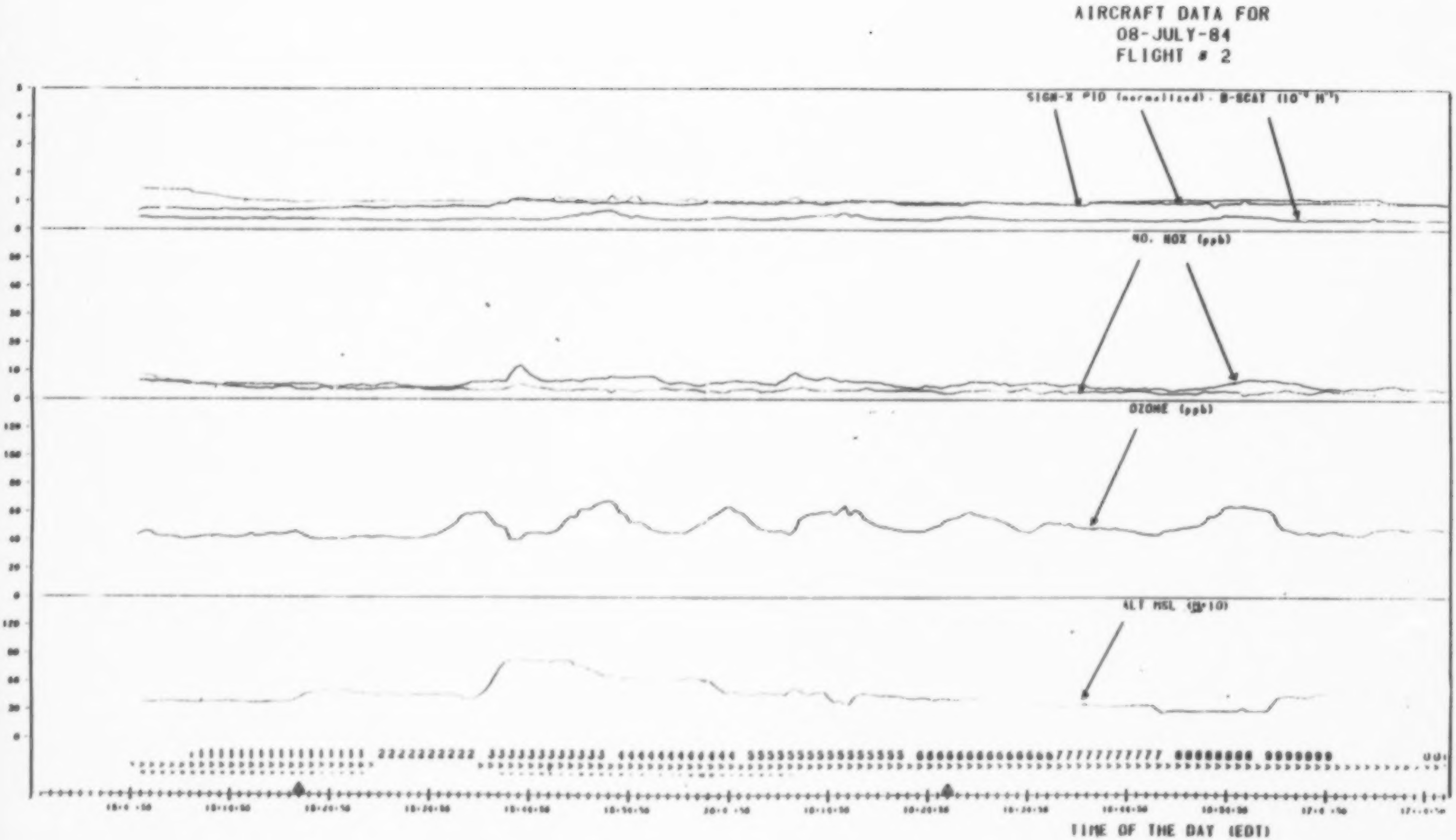


Figure 22(b): Aircraft Observations on July 8, 15-18:30 EDT

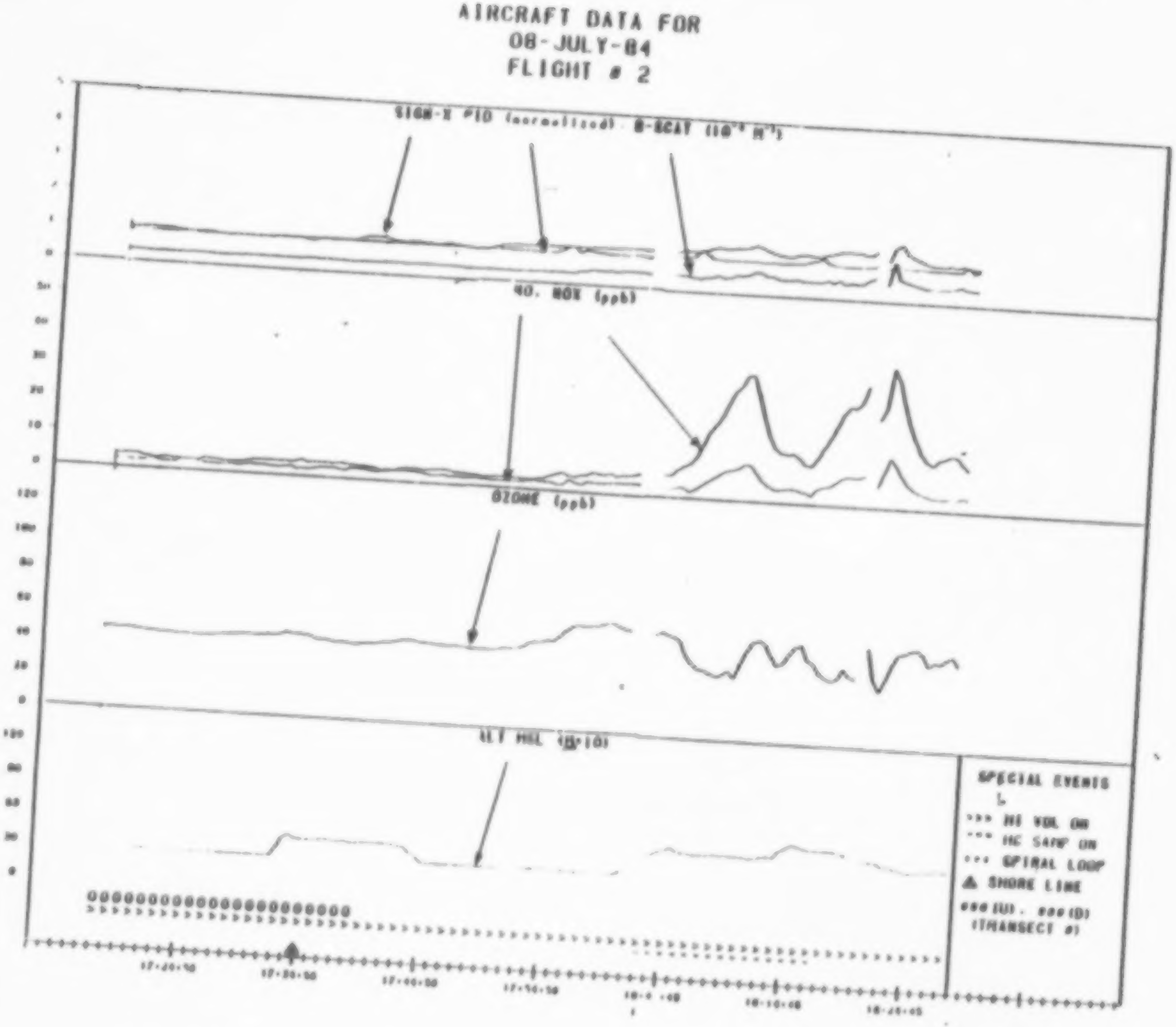


Figure 22(b): Aircraft Observations on July 8, 15-18:30 EDT (continued)

3.7. July 13

In several respects, this day was similar to July 8. A high-pressure cell was centered south of the lower Great Lakes in the general area of Kentucky, with a ridge extending northward to Moosonee. This resulted in light and variable winds over the Sarnia region during the study period, favoring the west-northwest direction in the morning, and becoming more southerly by early afternoon. A weak lake breeze developed, which had penetrated to Camlachie and the airport by about 14 - 15 hours. Wind speeds were in the 5 - 15 km h^{-1} range. In the morning, brown layers of polluted air were observed east of Sarnia. Mainly sunny skies prevailed, with afternoon temperatures in the mid-to upper twenties. The daytime relative humidity was in the 50-60% range, with a maximum hourly average solar radiation of 103 milliwatts per cm^2. For the period 0800 - 1700 EDT, the mixed layer height was initially around 100 m, then grew to about 1000 m by early afternoon. Near the end of the period, a stable ground layer developed.

Backward trajectories (48 hours) of air parcels over the Sarnia area during the study period indicate an air path from western Wisconsin, southeast to central Lake Michigan and then eastward to Sarnia. Forward air trajectories for the same period indicate an eastward movement. Ozone levels rose rapidly at the ground level monitoring stations during the morning, and exceedences of the air quality criterion (80 ppb) were observed at Wyoming and Courtright later in the afternoon (Figure 23). Both the upwind high volume samples taken on July 13, and nephelometer measurements (when the aircraft was clear of plumes) indicated that the air was relatively clean, with light scattering coefficient readings in the $0.5 - 1.0 \times 10^{-4}$ m^{-1} range, and sulfate and nitrate levels at 6.0 and 2.2 ug m^{-3} respectively - see Figure 25(a).

The morning flight (0924 - 1349 EDT) consisted of traverses in the general upwind (Figure 24(b)) and downwind (Figures 24(a) and 24(c) - (d)) direction of Sarnia. Unfortunately, only a partial data set was obtained, due to a data logger malfunction resulting from an unusually hard landing on return to the airport. However, all the ozone and nephelometer data were sucessfully recovered from the backup charts, and they indicate a definite ozone plume in the general downwind direction of Sarnia (Figures 24(a), (c) and (d)), with concentrations building up to values in excess of 80 pppb (Figure 24(c)) and then apparently tapering off again (Figure 24(d)). In these figures, approximately east of the Courtright area, there is a definite indication of lower ozone levels due to the presence of the generating station plumes, although this could not be confirmed with NO_x data (which were not available).

It is interesting to note that the ground level ozone data support the aircraft measurements and also suggest elevated ozone levels downwind of Sarnia, peaking at about 15 - 25 ppb above the background at the stations located about 20 km away, and tapering off to near -background levels farther afield. For example, taking the Merlin and Tiverton stations (approximately 100 km south and 200 km northeast of Sarnia respectively) as background stations during the sampling period, ozone values measured at 1200 - 1300 and 1300 -1400 EDT were: Merlin, 40 and 49 ppb; Tiverton (not shown on Figures 24(a) to (d)), 38 and 42 ppb. During this time, Camlachie reported 55 and 53 ppb ozone, while Wyoming reported 65 and 69 ppb.

By late afternoon, at the time of the second flight (1635 - 1834 EDT), regional winds were from the southwest, and background ozone levels (as measured at Merlin and Tiverton) were in the 50 - 60 ppb range. There was a definite indication in the aircraft data (taken at about 200 m above ground) of an ozone bulge (modified, as always, by the embedded generating station plume) peaking at about 40 ppb above the background levels, 20 - 40 km from Sarnia (Figures 24(e) and (f)). The results of traverse number 3 (Figure 24 (f)) are difficult to interpret, with ozone buildups observed over the lake just offshore, and near-background ozone levels farther inland, but they may be the result of the fairly complex flow field that must have occurred along the shoreline due to the presence of a lake breeze. A spiral carried out over the lake in between traverses 2 and 3 showed some vertical structure in the ozone concentrations at that location (Figure 25(b)). No hydrocarbon or high-volume samples were taken during the afternoon flight.

The ground level stations also strongly suggest an ozone plume downwind of Sarnia, with hourly average values at stations to the northeast significantly exceeding the values at Thedford and Tiverton, and the highest readings recorded at Wyoming. The relatively high hourly averages at Courtright, which should have been upwind of Sarnia during this period, are difficult to explain.

During the morning flight, three hydrocarbon samples were collected. Two of these were "upwind" samples, the first being collected at 0937 - 0953 EDT, over Lake Huron about 20 km to the north of Sarnia, and the second being collected during traverse 4 (Figure 24(b)) between 1132 and 1202. Another, downwind sample was collected during traverse 2 (Figure 24(a)). These are compared in the Table below with samples collected at Courtright and Camlachie during the period 9 - 12 EDT (during this period, Camlachie should have been approximately downwind of Sarnia, as is confirmed by the high observed hydrocarbon readings).

Location	Time EDT	Total HC (C_{3+})ug m^{-3}	Alkanes %	Alkenes %	Aromatics % (benzene)
Airplane upwind	0938-0953	56	68	3	27 (13)
	1132-1202	304	76	2	20 (5)
Courtright	0949-1049	71	82	3	9 (3)
	1049-1149	40	75	5	10 (4)
Airplane downwind	1020-1035	38	42	3	55 (19)
Camlachie	0900-1000	423	66	3	24 (13)
	1000-1100	499	65	4	26 (14)

The high levels of hydrocarbons in the "upwind" aircraft sample collected between 1132 and 1202 are difficult to explain - an error in aircraft sample labelling may have occurred. Using the ground based data only (i.e. Courtright taken as approximately upwind, and Camlachie as downwind), it seems that Sarnia emissions are enriching the downwind air parcels with all species, but especially the aromatics. It is interesting that all the data collected in the morning show relatively high levels of the photochemically reactive alkenes and alkylbenzenes in the area. Some readings from the ozone precursor monitor were available at Camlachie (1010 - 1110 hours), and showed high ozone precursor values (20 ppb), confirming the oxidant-forming potential of the air in the area.

It should also be noted that an inspection of the hydrocarbon and nitrogen oxides monitoring data collected during the early morning at Sarnia stations generally showed values higher than the monthly average values for the same hours, due to the light winds at the time.

During the sampling period, no measurements are reported from the York University formaldehyde, hydrogen peroxide and nitric oxide monitors. The TAGA unit at Courtright carried out some sampling for aldehydes, ketones, acetates and alcohols in the late afternoon. Aldehydes were in the 1 - 2 ppb range; ketones were generally less than 1 or 2 ppb, with the exception of acetone (3 - 7 ppb); acetates were less than 1 ppb; and methanol, ethanol and butanol were found at 2-4 ppb concentrations, with propanol at about 10 ppb.

To summarize: this day was meteorologically similar to July 8, except that a better definition of upwind and downwind directions could be obtained. The aircraft and ground-level data indicate a definite ozone plume downwind of Sarnia (on July 8, due to the light and variable winds, only patches of ozone were observed in the Sarnia area), with peak ozone levels of about 10 ppb or more above the regional background values, apparently building up to a maximum at about 20 - 40 km from Sarnia, and then tapering off again to near-regional values. The ambient hydrocarbons in the morning were found to have relatively high concentrations of the photochemically reactive alkenes and alkylbenzenes, and the ozone-forming potential of the atmosphere was confirmed by some limited ozone precursor monitor data.

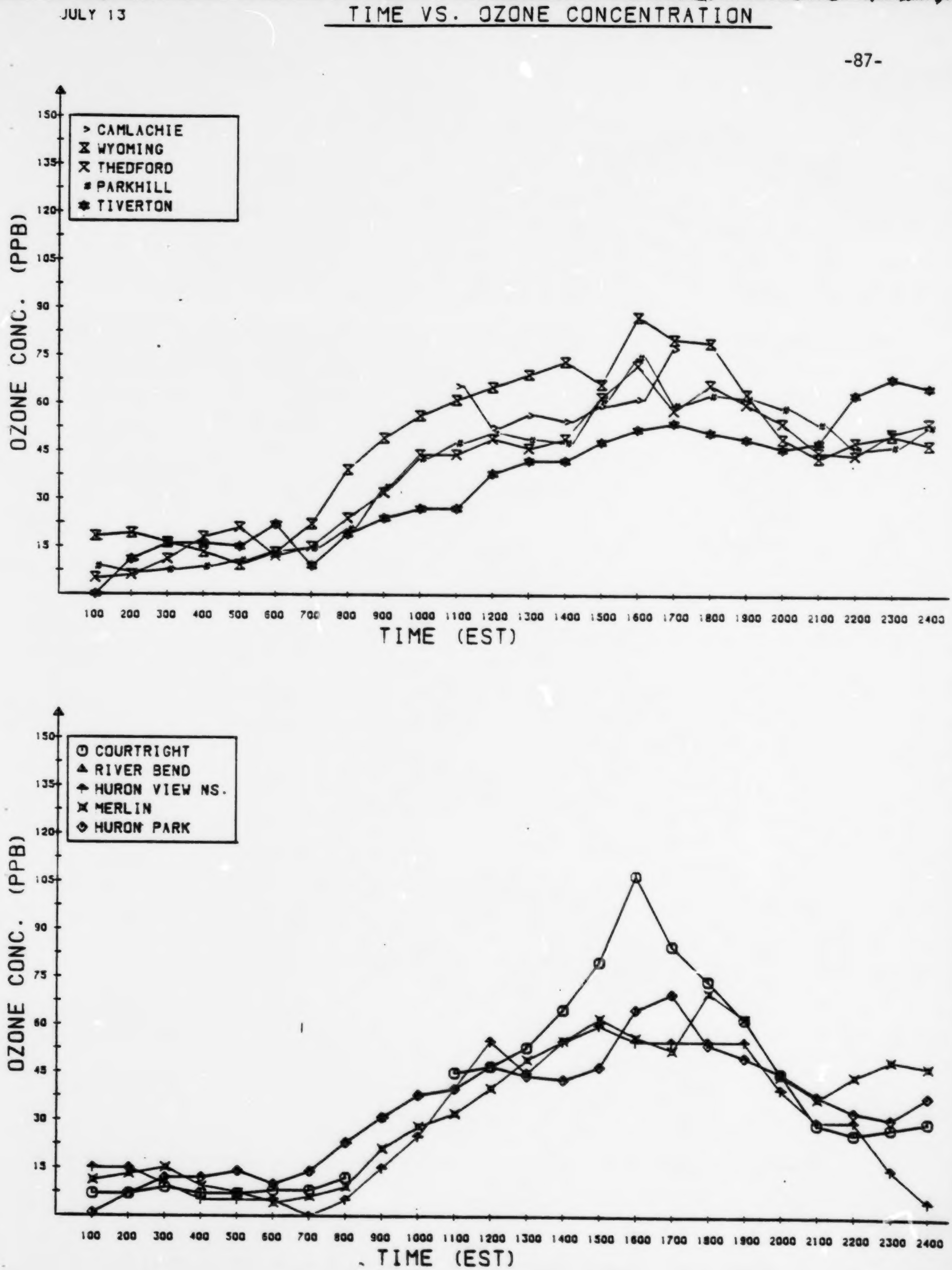


Figure 23: Diurnal Variation of Ozone Concentrations in the Sarnia Area, July 13

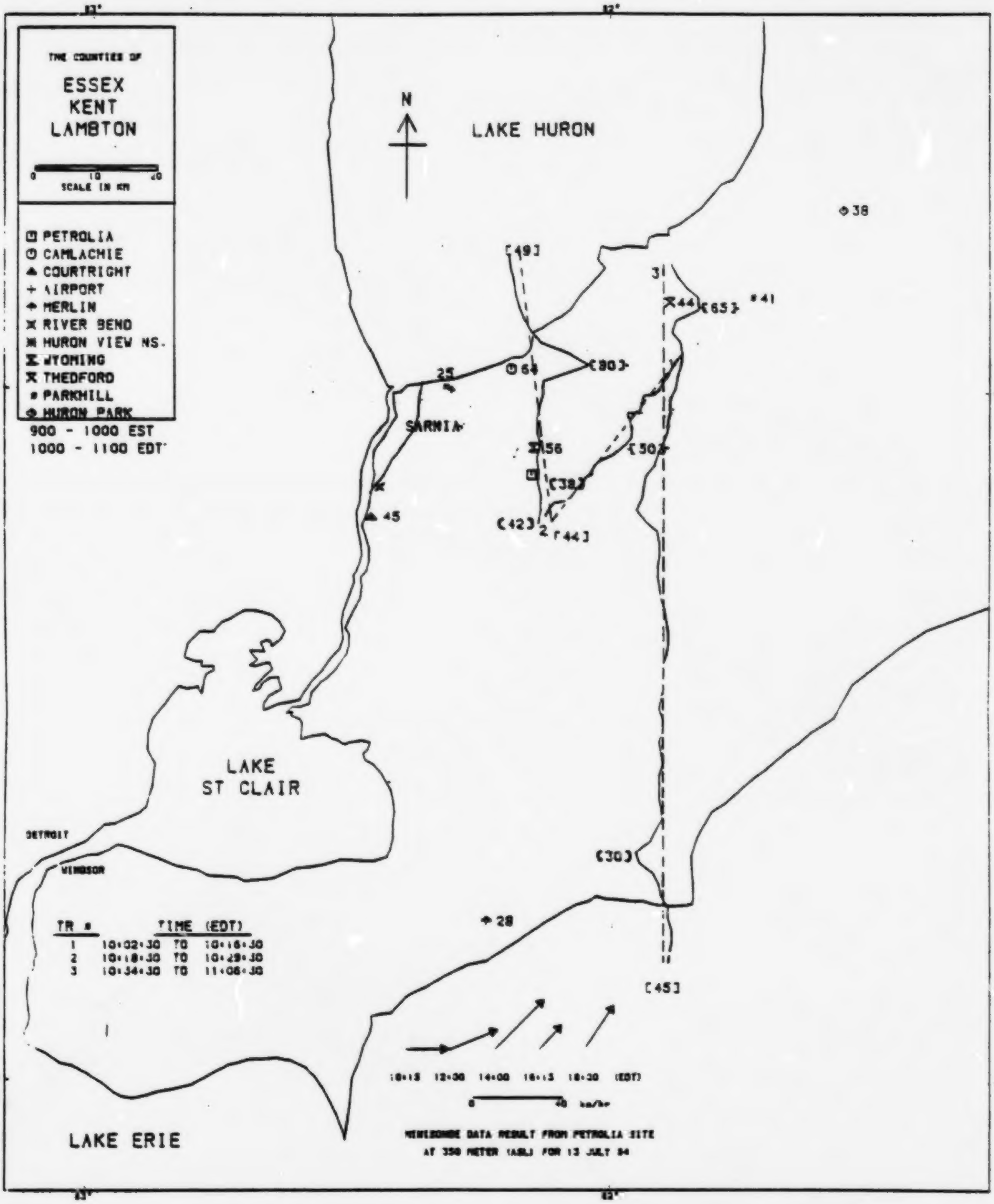

83°
82°
43°
42°
THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
20
SCALE IN KM
▣ PETROLIA
○ CAMLACHIE
▲ COURTRIGHT
+ AIRPORT
✦ MERLIN
✕ RIVER BEND
✱ HURON VIEW NS.
Σ WYOMING
✕ THEDFORD
* PARKHILL
◆ HURON PARK
900 - 1000 EST
1000 - 1100 EDT
N
LAKE HURON
[49]
3
44
[65]
*41
◆38
25
○64
[80]
SARNIA
56
[50]
[38]
45
[42]
2
[44]
LAKE ST CLAIR
DETROIT
WINDSOR
[30]
✦28
[45]
TR #
TIME (EDT)
1 10:02:30 TO 10:16:30
2 10:18:30 TO 10:29:30
3 10:34:30 TO 11:06:30
1
10:15
12:00
14:00
16:15
18:30
(EDT)
0
40
km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 350 METER (ASL) FOR 13 JULY 84
LAKE ERIE

Figure 24(a): Ozone Observations in the Sarnia Area on July 13, 10-11 EDT

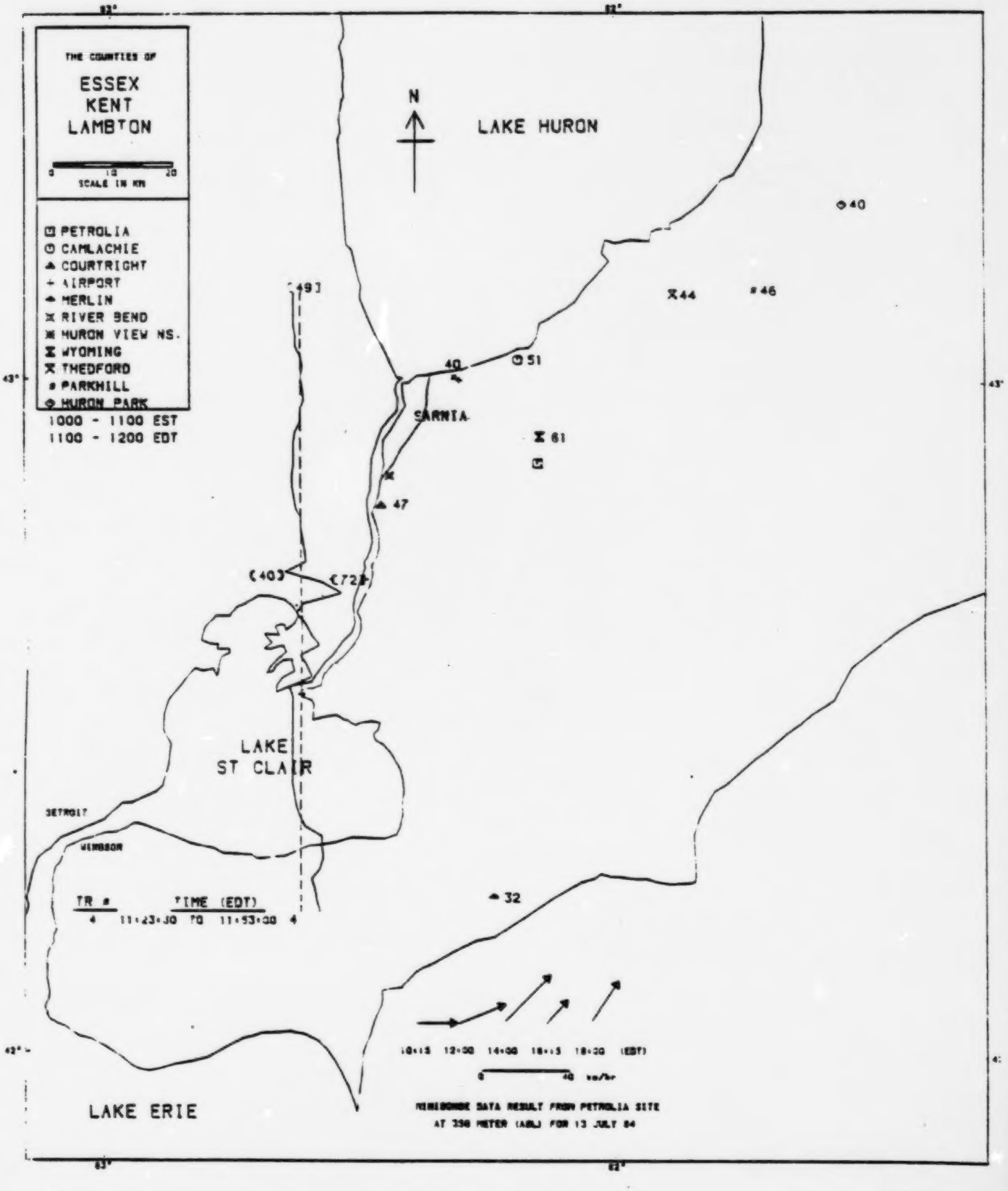

83°
82°
THE COUNTIES OF
ESSEX
KENT
LAMBTON
0 10 20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
1000 - 1100 EST
1100 - 1200 EDT
N
LAKE HURON
40
44
46
[49]
40
51
SARNIA
61
47
(40)
(72)
LAKE
ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
4 11:23:30 TO 11:53:30 4
32
10:15 12:00 14:00 16:15 18:30 (EDT)
0 40 km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 350 METER (AGL) FOR 13 JULY 84
LAKE ERIE
43°
42°

Figure 24(b): Ozone Observations in the Sarnia Area on July 13, 11-12 EDT

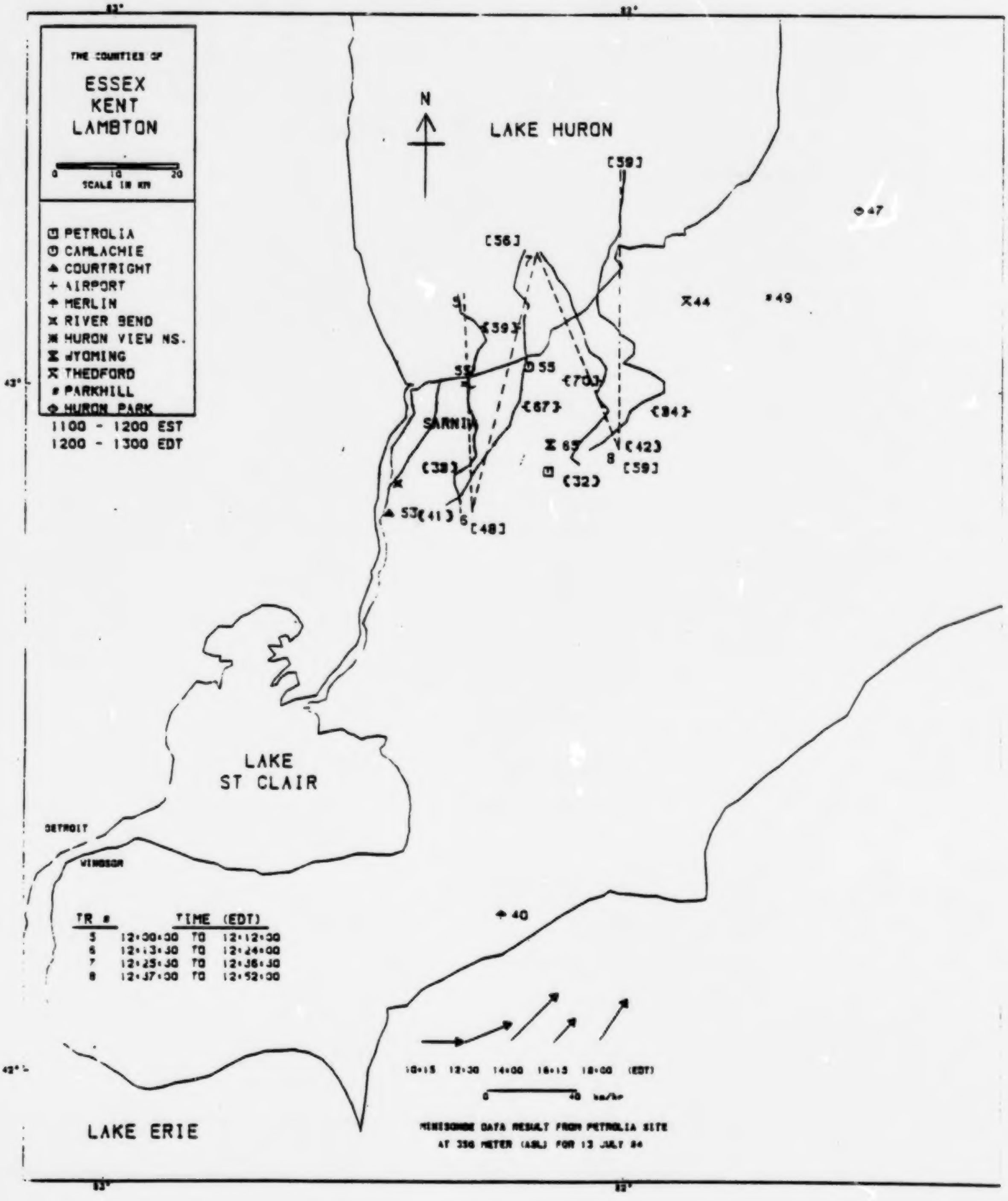

THE COUNTIES OF
ESSEX
KENT
LAMBTON
0 10 20
SCALE IN KM
□ PETROLIA
⊙ CAMLACHIE
▲ COURTRIGHT
+ AIRPORT
✦ MERLIN
✕ RIVER BEND
✱ HURON VIEW NS.
Σ WYOMING
⌆ THEDFORD
# PARKHILL
◇ HURON PARK
1100 - 1200 EST
1200 - 1300 EDT
N
LAKE HURON
[59]
⊙47
[56]
7
5
[39]
⌆44
#49
55
⊙55
[70]
[84]
[67]
SARNIA
Σ 65
[42]
8
[59]
[38]
□
[32]
▲ 53
[41]
6
[48]
LAKE ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
5 12:00:00 TO 12:12:00
6 12:13:30 TO 12:24:00
7 12:25:30 TO 12:36:30
8 12:37:00 TO 12:52:00
✦40
10:15 12:30 14:00 16:15 18:00 (EDT)
0 40 km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 350 METER (ASL) FOR 13 JULY 84
LAKE ERIE
83°
82°
43°
42°

Figure 24(c): Ozone Observations in the Sarnia Area on July 13, 12-13 EDT

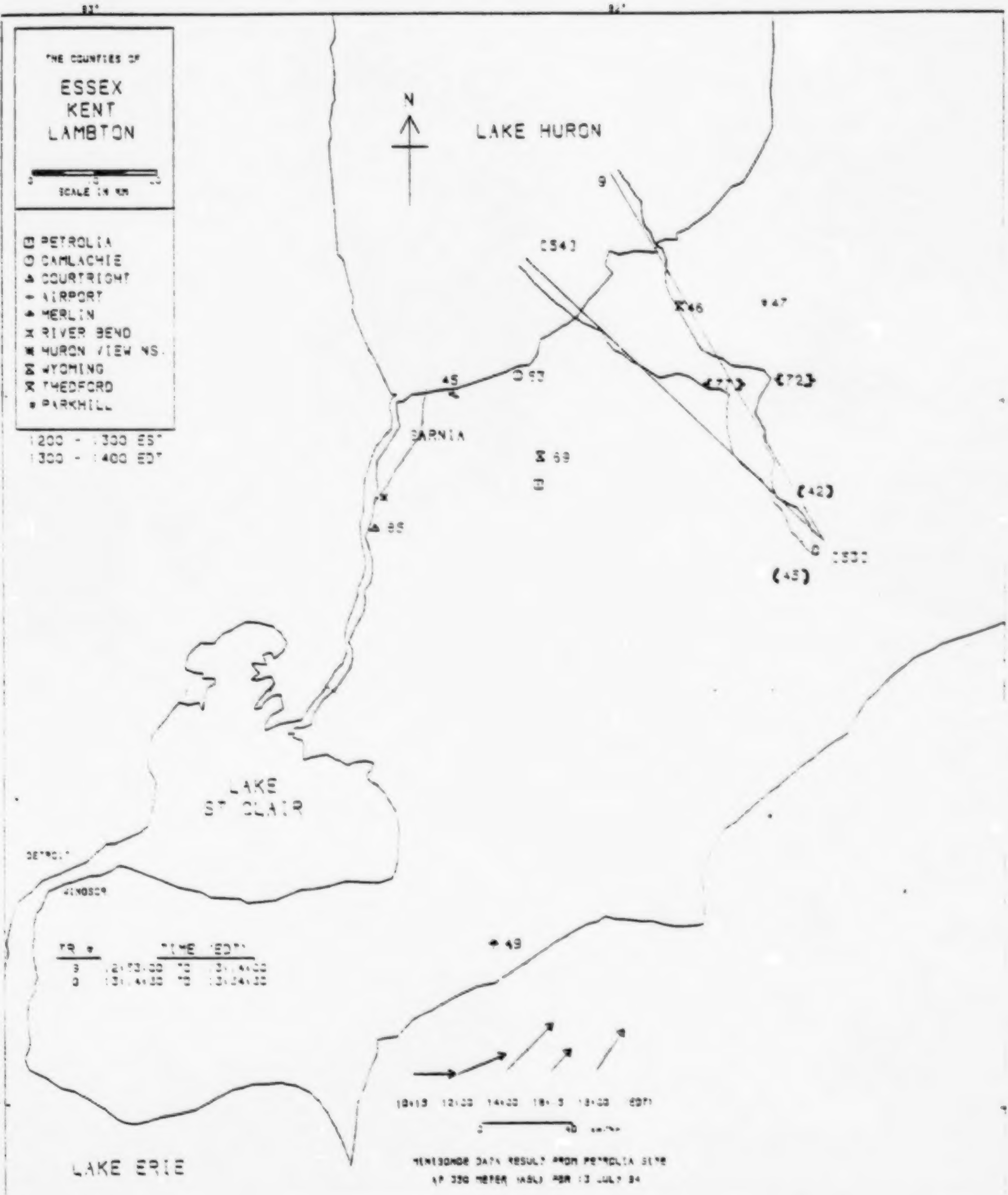

THE COUNTIES OF
ESSEX
KENT
LAMBTON
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS.
WYOMING
THEDFORD
PARKHILL
1200 - 1300 EST
1300 - 1400 EDT
N
LAKE HURON
9
[54]
46
47
45
53
[77]
[72]
SARNIA
69
[42]
[53]
[45]
85
LAKE ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
9 12:53:00 TO 13:14:00
0 13:14:30 TO 13:24:30
49
10:13 12:00 14:00 16:15 18:00 (EDT)
0 40 km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 330 METER (ASL) FOR 13 JULY 84
LAKE ERIE

Figure 24(d): Ozone Observations in the Sarnia Area on July 13, 13-14 EDT

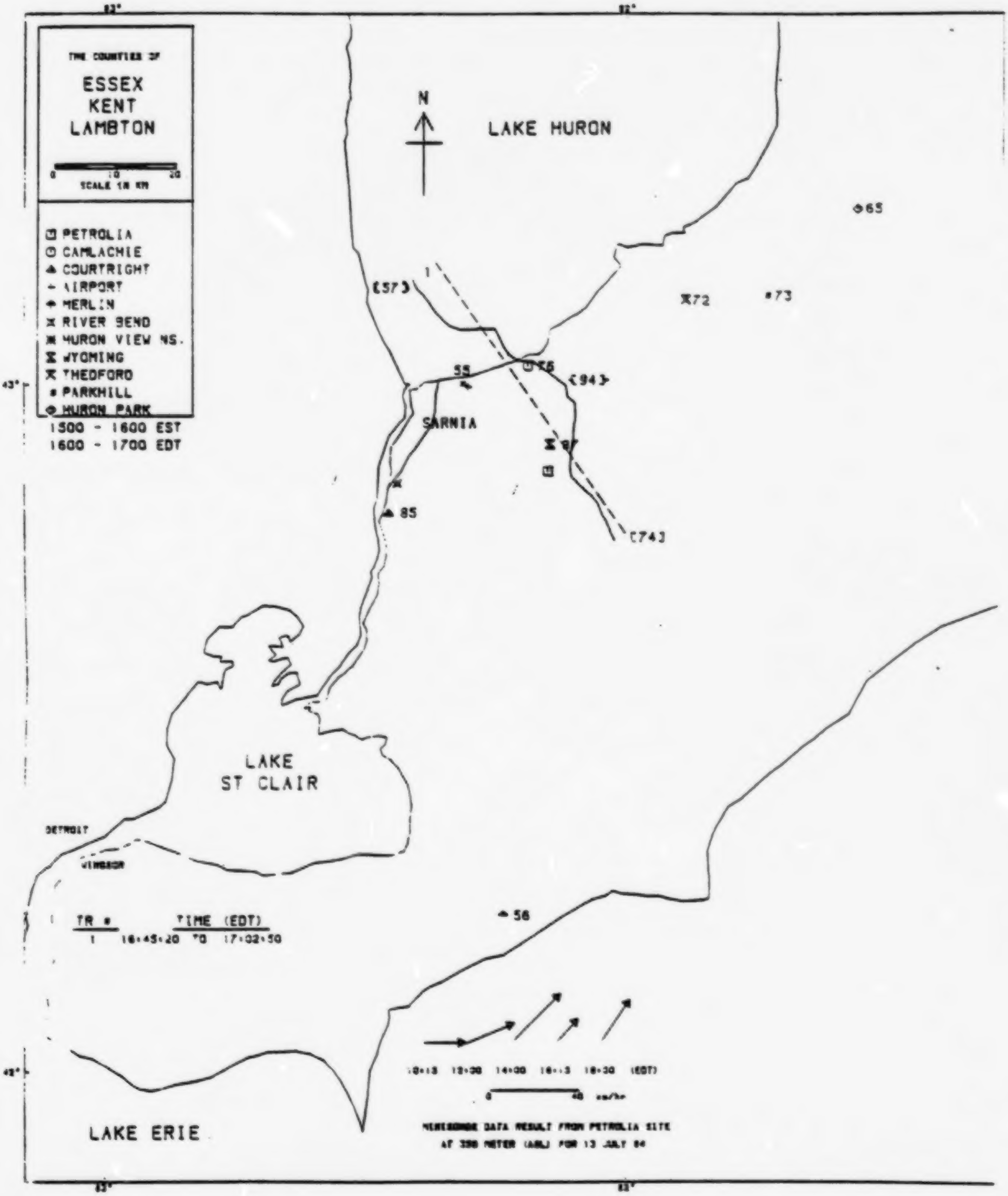

THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW HS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
1500 - 1600 EST
1600 - 1700 EDT
N
LAKE HURON
65
72
73
[57]
1
55
76
[94]
SARNIA
87
85
[74]
LAKE ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
1
16:45:20 TO 17:02:50
56
12:30
14:00
16:30
(EDT)
0
40
km/hr
AT 330 METER (AGL) FOR 13 JULY 84
LAKE ERIE
43°
42°
83°
82°

Figure 24(e): Ozone Observations in the Sarnia Area on July 13, 16-17 EDT

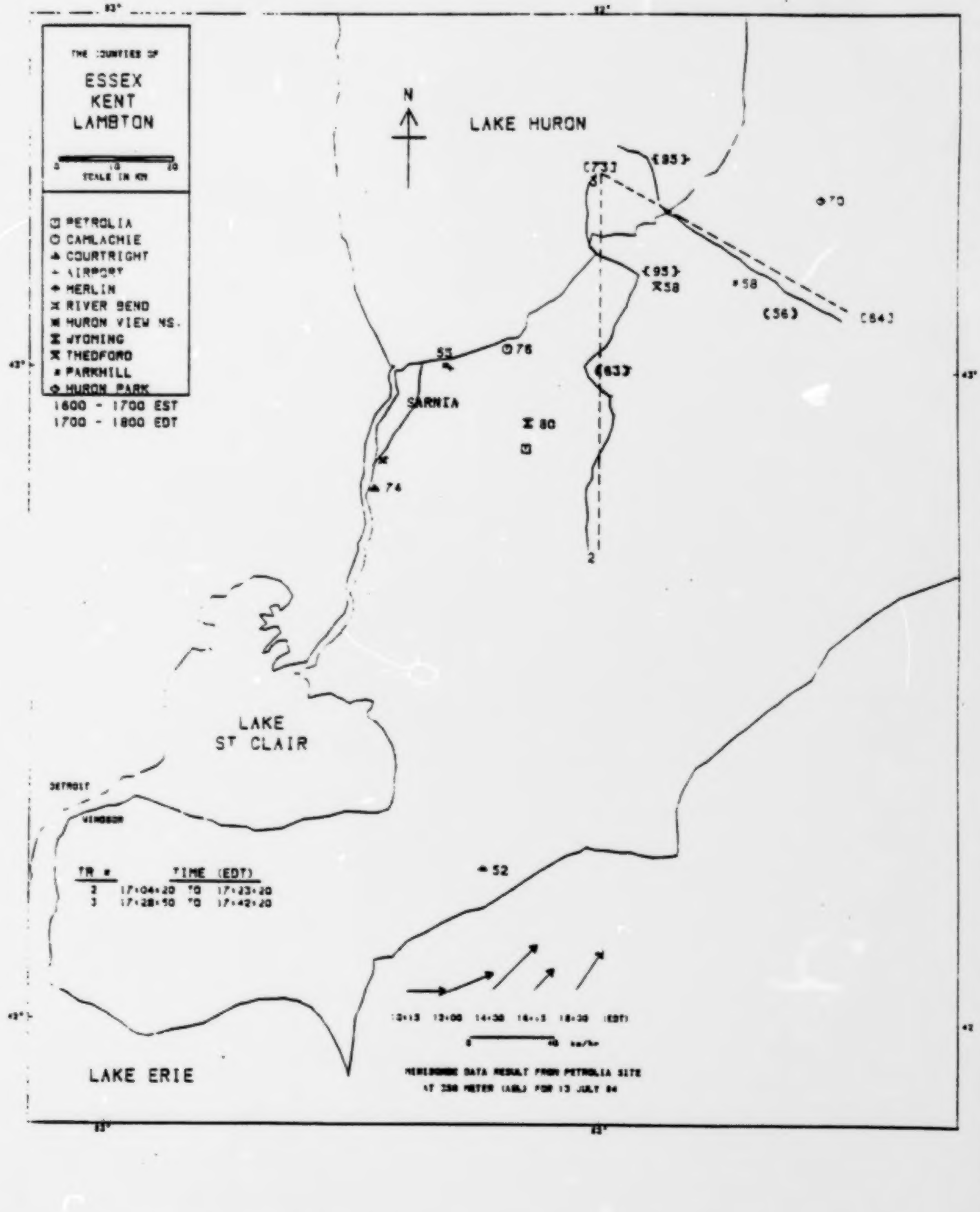

THE COUNTIES OF
ESSEX
KENT
LAMBTON
0 10 20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
1600 - 1700 EST
1700 - 1800 EDT
N
LAKE HURON
[73]
{85}
70
{95}
58
58
[56]
[64]
55
76
{63}
SARNIA
80
74
2
LAKE
ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
2 17:04:20 TO 17:23:20
3 17:28:50 TO 17:42:20
52
12:15 13:00 14:30 16:15 18:30 (EDT)
0 40 km/hr
AIRSONDE DATA RESULT FROM PETROLIA SITE
AT 330 METER (AGL) FOR 13 JULY 84
LAKE ERIE
83°
82°
43°
42°

Figure 24(f): Ozone Observations in the Sarnia Area on July 13, 17-18 EDT

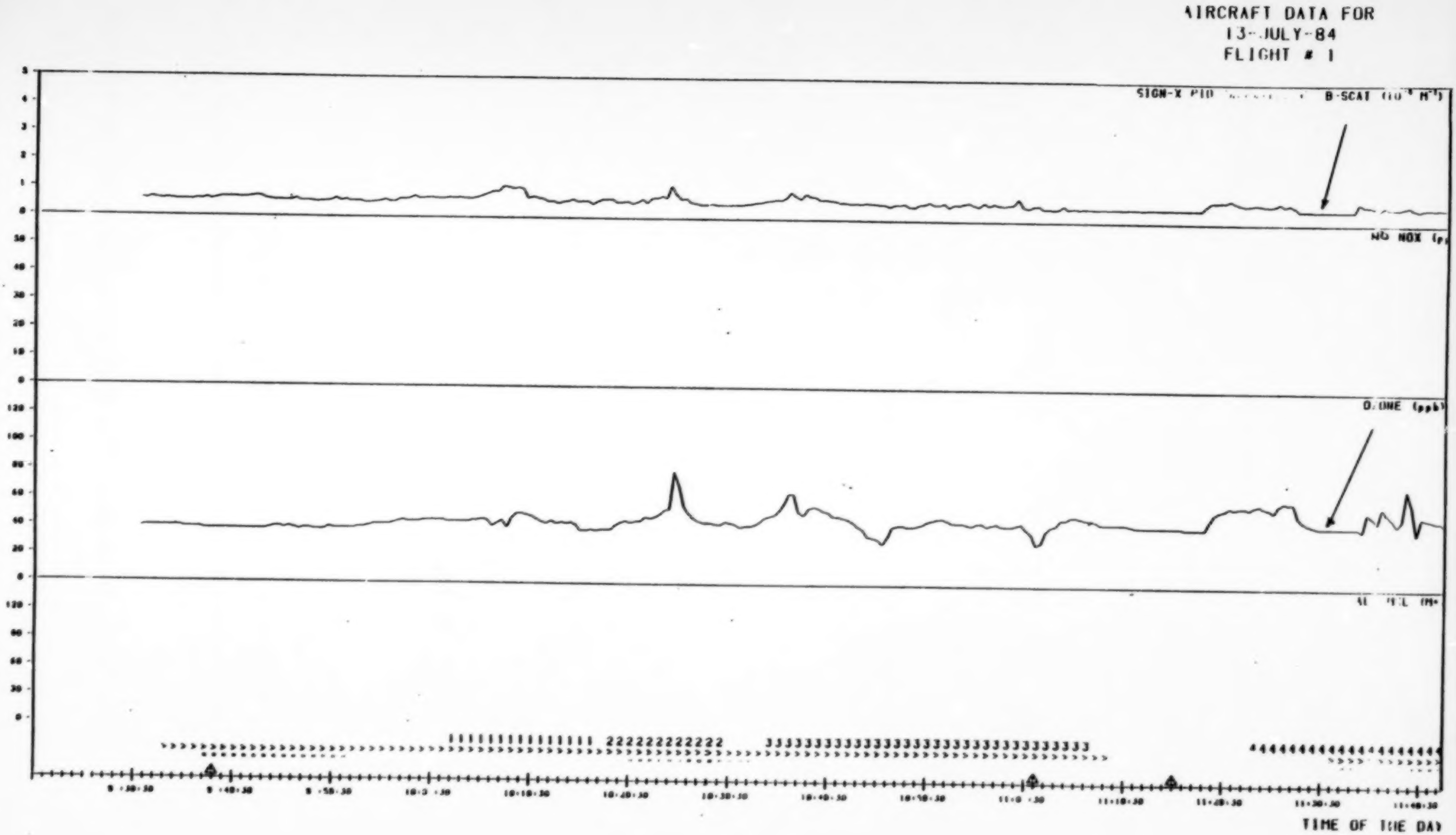


Figure 25(a): Aircraft Observations on July 13, 9-14 EDT

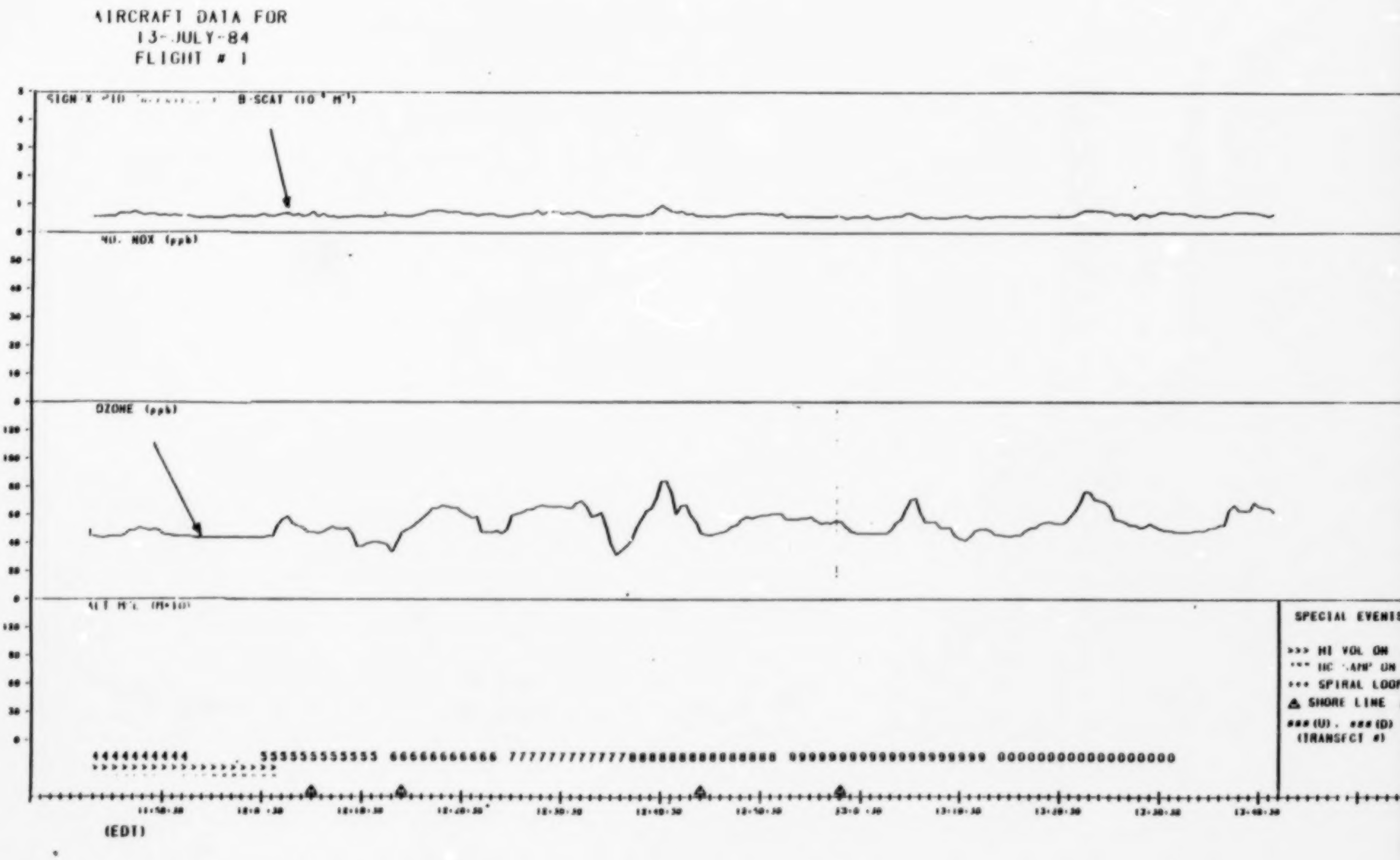


Figure 25(a): Aircraft Observations on July 13, 9-14 EDT (continued)

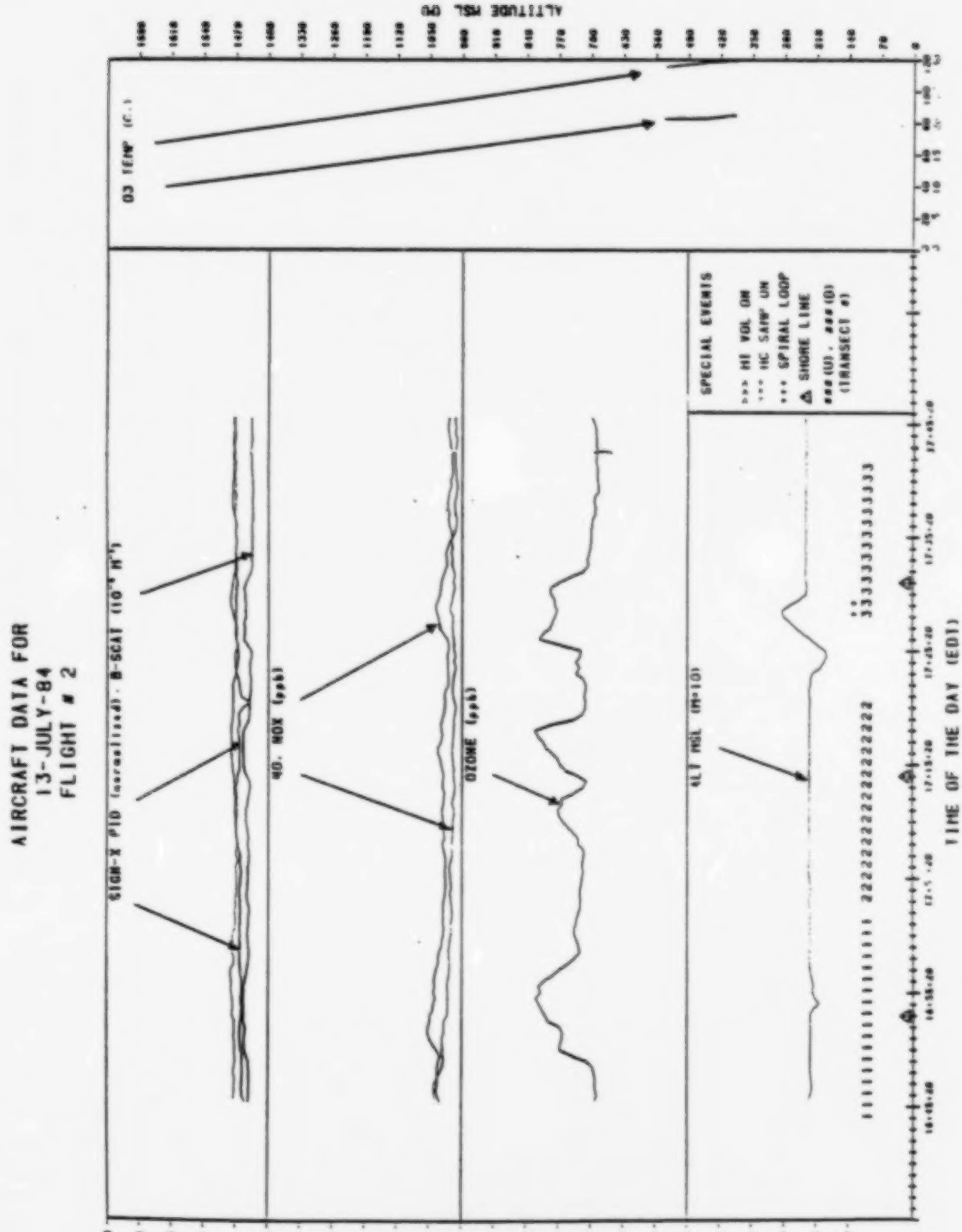


Figure 25(b): Aircraft Observations on July 13, 16:30-18:00 EDT

3.8. July 14

On July 14, the previously - mentioned quasi-stationary high pressure system was centered in the vicinity of Kentucky - West Virginia. To the north, a quasi-stationary frontal system extended in an east-west line through the upper Great Lakes. As a result, the Sarnia region remained in a post-ridge/pre-warm front situation, and experienced gradient winds with a southerly component. During the period 0900-1200 EDT, when the aircraft flights were conducted, winds were from the west-southwest, with speeds in the 10-20 km h^{-1} range. Scattered clouds occurred, with temperatures in the mid-to upper twenties. The maximum solar radiation rose to slightly in excess of 80 milliwatts cm^{-2} (by noon); the surface relative humidity was in the 50-60% range for most of the flight period (dropping from near 70% at the time of takeoff, around 0900). The minisonde data suggest an initial mixed layer of 150 m, gradually increasing to about 1000 m by noon. In the early morning, until 0800 hours, a brown haze was visible over the Sarnia area, with portions advected over Lake Huron, and other portions going off in an easterly direction.

During the study period, forward trajectories from Sarnia show a northeastward movement. On the other hand, backward trajectories (48 hours) of air parcels over the Sarnia area indicate slow movement from Illinois northeastwards.

Because of the more southerly origins of the air entering the study area on this day (as compared to July 13), a higher upwind loading of pollutants was observed, as well as a poorer visibility (b_{scat} was about 1×10^{-4} m^{-1} or greater) and greater sulfate and nitrate levels (54 and 20 ug m^{-3} - however, these levels may be so high because portions of the Detroit/Windsor plume may have been sampled during part of the upwind traverse). During the time of the flight, ozone levels increased rapidly across the network (Figure 26), and by late afternoon had exceeded the provincial hourly air quality criterion of 80 ppb at most stations.

The rapid change in meteorological conditions in the period immediately before, and during the first hour or so, of the study (i.e. rapid growth of the mixing layer, winds changing from southerly to west-southwesterly), makes the data interpretation somewhat difficult for this day. With the exception of a spiral carried out at the end of the flight, an altitude of about 200 m above ground level was maintained by the aircraft. Since the sampling aloft was started soon after 0900 hours EDT, for the first two (possibly three) traverses (judging from the minisonde data at Camlachie and Petrolia) the aircraft was probably in relatively stable air, above the mixing layer. It is interesting to note that during this portion of the flight, the ozone measurements aloft were quite patchy (Figures 27(a) and 28), due to scavenging by NO plumes (from the generating stations near Courtright or possibly other urban/industrial sources in the Sarnia area). Outside of these ozone "dips" caused by NO scavenging, levels in excess of 80 ppb were encountered aloft. However, at the same time, ground level hourly average ozone values were considerably lower and fairly uniform across the network, at about 45 ppb. From these observations it is concluded that a significant portion of the rapid ozone increase at ground level during the morning hours of July 14 (Figure 26) was due to mixing downwards of ozone -rich air layers from aloft. Furthermore, although a preliminary glance at Figure 27(a) might suggest the presence of ozone plumes attributable to Sarnia, a closer inspection of the aircraft data (Figure 28) indicates that the observed structure in the ozone profiles is largely due to scavenging by NO_x plumes imbedded in a reasonably uniform, background air mass, with fairly high ozone loadings. In traverses 2 and 3, there is evidence for some ozone buildup over Lake Huron, however, which could possibly be due to air polluted earlier by Sarnia emissions, and carried out over the lake by the early morning southerly winds.

Traverses 4 and 5 (Figures 27(b) and (c)) were flown clear of the Sarnia plume, within the mixing layer. There is now much closer agreement between the aircraft and ground-level ozone measurements, and an indication of an ozone buildup over Lake Erie. It is not clear whether this buildup is due to a Windsor - Detroit plume, or to the occurrence of elevated ozone values in relatively stable air layers over the water. Over land, ozone concentrations were much more uniform, although the nephelometer and NO_x analyser data indicate the presence of some residual plumes (possibly from Windsor - Detroit) to the south of Sarnia (Figure 28).

The last two traverses, which were carried out downwind of Sarnia (Figure 27(d)), are difficult to interpret. There is evidence of fairly localized ozone buildups due to Sarnia near the southern shoreline of Lake Huron, as well as scavenging by generating station plumes farther to the south. Traverse 7 indicates an appreciable ozone buildup over Lake Huron, but a spiral flown nearby, just after the completion of this traverse, showed that the aircraft had probably intersected a fairly localized high-concentration ozone layer, about 100 m thick, located near the top of a stable air layer over the lake (again, this ozone may have been formed from Sarnia emissions, carried out over the lake on early morning southerly winds) - see Figure 28.

The hydrocarbon monitoring results on this day are interesting, because the wind was blowing Sarnia emissions towards the Camlachie monitoring site. Hydrocarbon observations at Camlachie, Courtright, and aboard the aircraft are tabulated below, for the periods when there was an overlap of observations from at least two locations.

Location	Time EDT	Total HC (C_{3+})ug m^{-3}	Alkanes %	Alkenes %	Aromatics %
Aircraft	0912-0941	84	86	0.2	13
	0943-1013	79	77	0.1	22
Courtright	0854-0954	194	69	2.9	21
	0954-1054	149	74	2.8	16
Camlachie	1048-1148	336	87	3.3	8.0
	1148-1248	153	81	1.2	15
Courtright	1054-1154	79	81	1.0	11
	1154-1254	60	78	1.1	10
Aircraft	1018-1048	45	43	0.2	56

The earlier samples collected aboard the aircraft (downwind, before 1013 hours) and at Courtright (before 1054 hours) are of similar composition, except that the concentrations of alkenes is significantly higher at Courtright. In fact, the hydrocarbon levels at Courtright are surprisingly high, even though according to local wind measurements, the Sarnia emissions should have been blown in a northerly to northeasterly direction (away from the site) during the preceding twelve hours or more. The early Courtright measurements resemble the later Camlachie hydrocarbon data, collected between 1048 and 1248 hours, downwind of Sarnia suggesting that upwind (possibly Detroit) emissions may be affecting the entire area.

During the second period, when data are available for Camlachie, both Courtright and the aircraft were collecting samples clear of the Sarnia plume, and observing considerably lower levels than Camlachie. The Camlachie measurements however may still have been largely influenced by the same air parcel that was over Courtright (before 1054), rather than Sarnia emissions. They show the ambient hydrocarbons to consist largely of alkanes (about 80% by weight), followed by aromatics (about 10%, roughly one-half being benzene) and alkenes (1-3%). The aircraft samples collected downwind (0912 - 1013) show considerably lower alkene levels (about one-tenth the percentage of the ground level samples). The aircraft sample collected clear of Sarnia emissions (1018 - 1048) shows a surprisingly high level of aromatics (56%), and may have been somehow contaminated.

Because of the relatively high levels of alkenes measured at Camlachie during the period 1048 - 1248, the concurrent NO_x and ozone precursor monitor results were examined. Levels of NO_x during the hourly periods 1040 - 1140 and 1140 - 1240 were 0.02 ppm, and below detection limits, respectively: ozone precursor levels were 11 and 18 ppb respectively. Earlier in the day (0854 - 1054), the hydrocaron levels, and composition of the mixture, at Courtright was found to be similar to that at Camlachie (1048 - 1248). However, NO_x levels were higher (0.04 and 0.05 ppm during the hours 0849 - 0949 and 0949 - 1049 respectively). It is interesting that the ozone precursor values at Courtright (27 and 25 ppb respectively during the above hours) were considerably higher than the Camlachie ozone precursors, suggesting that in the Sarnia area, oxidants formation may be NO_x - limited.

No measurements are available from the York University monitoring site at Camlachie during the period of interest. The TAGA unit at Courtright did collect a reasonably complete set of samples, however, of aldehydes (other than formaldehyde), ketones, acetates and alcohols, indicating levels of 1 - 2 ppb or less, with some compounds (acetone, methanol, propanol) showing occasional excursions in excess of 5 ppb.

The continuous monitoring urban sites, which were operational on July 14, do not indicate any unusually high hydrocarbon or NO_x levels in the morning. It is interesting to note that the monitoring sites at Merlin and Tiverton, which should have been clear of the Sarnia plume, were recording relatively low ozone values during the period of interest (around 50 - 60 ppb), compared to some of the stations downwind of Sarnia (especially during the 1100 - 1200 EDT period - see Figure 27(d)), suggesting an ozone contribution attributable to Sarnia emissions. Furthermore, the increase in ozone levels between 0900 and 1200 EDT, when the mixing layer was deepening, was considerably larger at the downwind sites (about 30 - 50 ppb), suggesting that a significant, if not the major, portion of the ozone reservoir aloft in the study area was due to Sarnia.

In summary, both the aircraft and ground level data on July 14 suggest some contribution from Sarnia to the regional ozone levels, although this contribution is difficult to define. Further, a large ozone reservoir aloft, which may have had a significant contribution from local sources, is suggested in the measurements, which strongly influenced the variation of the ground level ozone concentrations during the morning hours. Although the intensity of solar radiation was not as high on this day as some others, the provincial hourly air quality criterion for ozone was exceeded at most stations in the study area by late afternoon. The previous air parcel history (from relatively polluted upwind areas) no doubt provides at least part of the explanation for the higher regional ozone levels, with Sarnia emissions adding to these.

JULY 14

TIME VS. OZONE CONCENTRATION

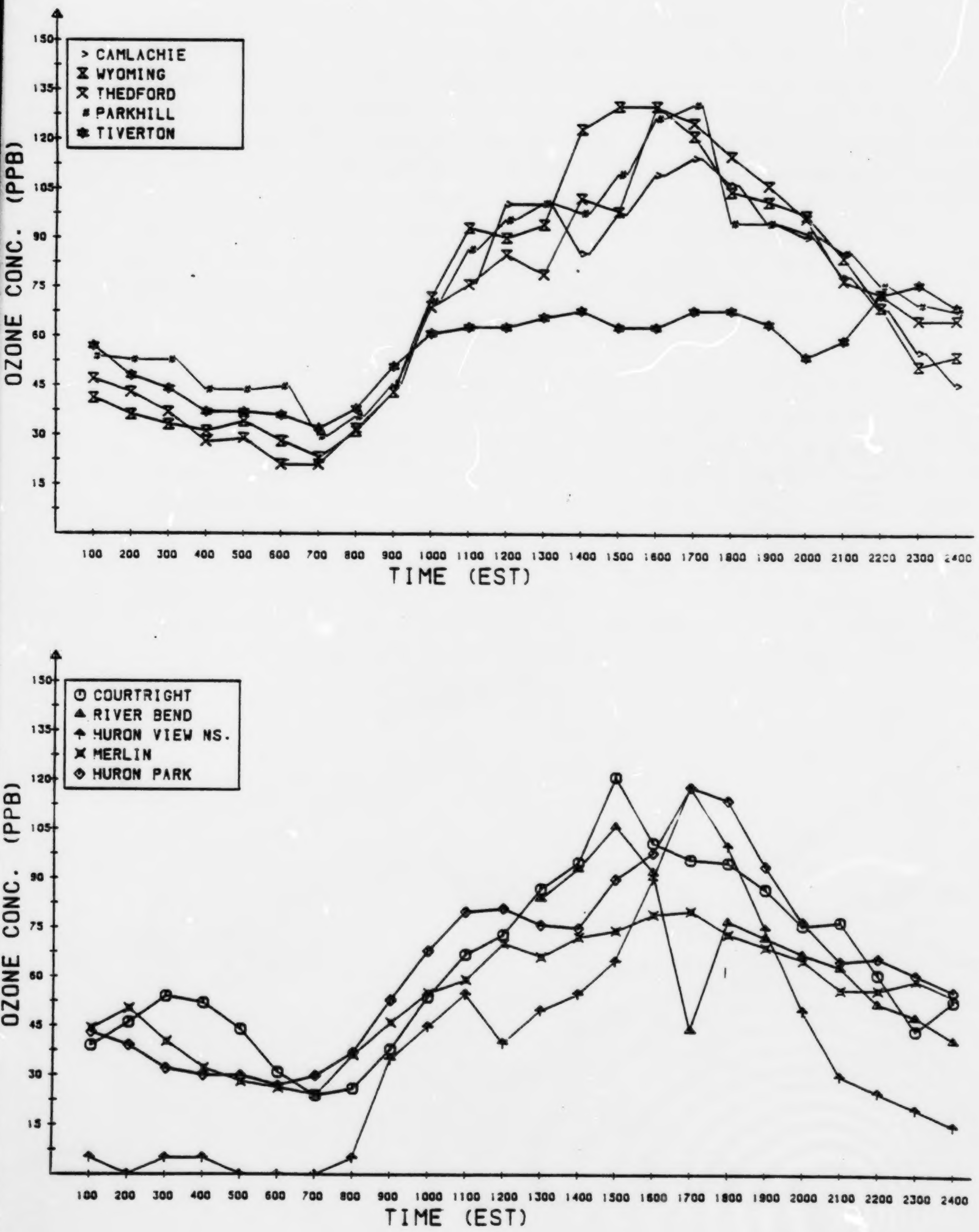


Figure 26: Diurnal Variation of Ozone Concentrations in the Sarnia Area, July 14

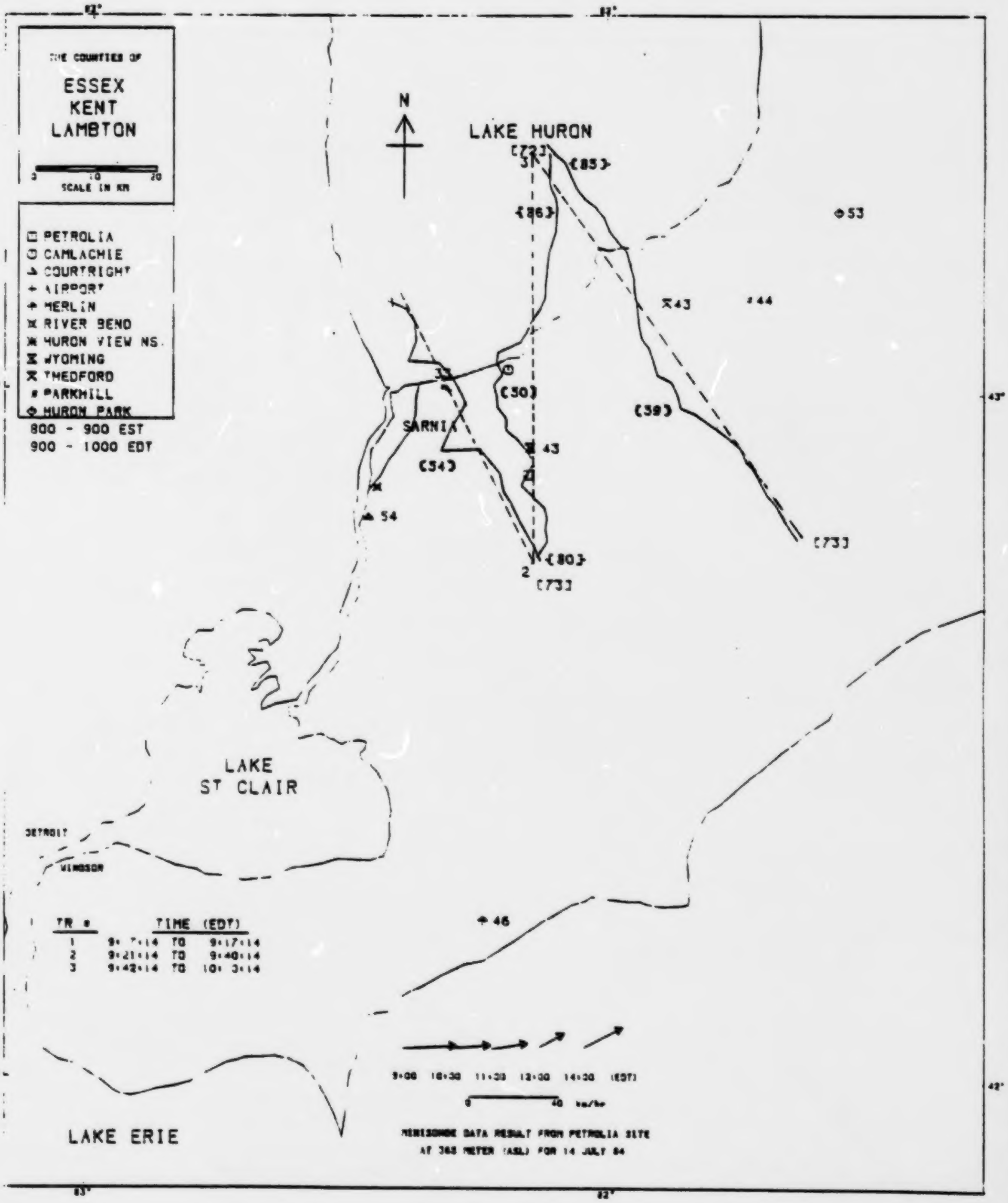

THE COUNTIES OF
ESSEX
KENT
LAMBTON
0 10 20
SCALE IN KM
□ PETROLIA
○ CAMLACHIE
▲ COURTRIGHT
+ AIRPORT
✦ MERLIN
⌘ RIVER BEND
✱ HURON VIEW NS.
⧗ WYOMING
⧗ THEDFORD
• PARKHILL
◇ HURON PARK
800 - 900 EST
900 - 1000 EDT
N
LAKE HURON
[72]
3
[85]
[86]
53
43
44
3
[50]
[39]
SARNIA
43
[54]
54
[80]
1
2
[73]
[73]
LAKE ST CLAIR
DETROIT
WINDSOR
46
TR #
TIME (EDT)
1 9: 7:14 TO 9:17:14
2 9:21:14 TO 9:40:14
3 9:42:14 TO 10: 3:14
9:00 10:30 11:30 12:00 14:30 (EDT)
0 40 km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 365 METER (ASL) FOR 14 JULY 84
LAKE ERIE
83°
82°
43°
42°

Figure 27(a): Ozone Observations in the Sarnia Area on July 14, 9-10 EDT

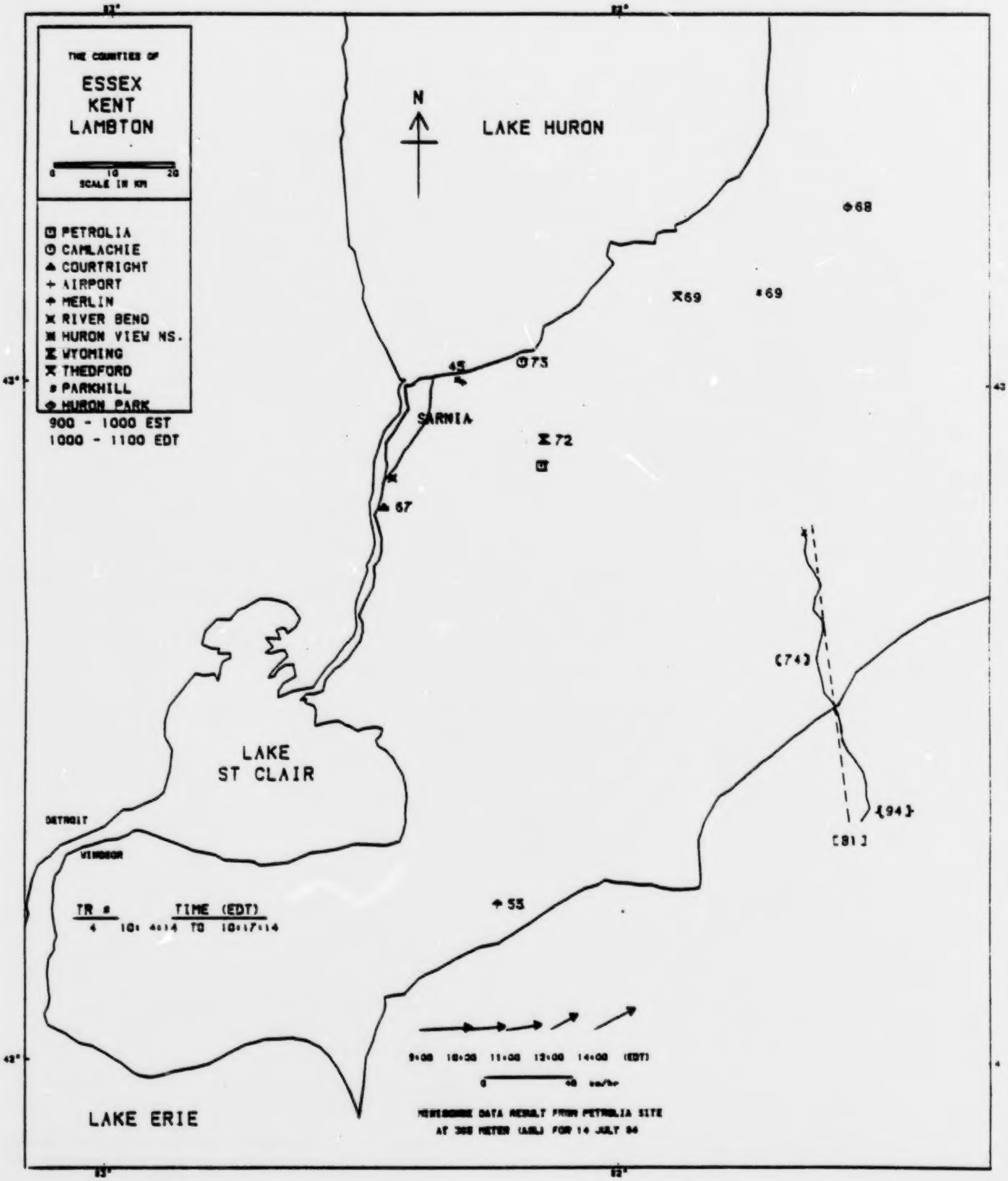

THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
900 - 1000 EST
1000 - 1100 EDT
N
LAKE HURON
68
69
69
45
73
SARNIA
72
67
(74)
(94)
(81)
LAKE ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
4
10:14:14 TO 10:17:14
55
9:00
10:00
11:00
12:00
14:00
(EDT)
0
40
km/hr
DATA RESULT FROM PETROLIA SITE
AT 300 METER (ASL) FOR 14 JULY 84
LAKE ERIE
43°
42°
83°
82°

Figure 27(b): Ozone Observations in the Sarnia Area on July 14, 10-11 EDT.

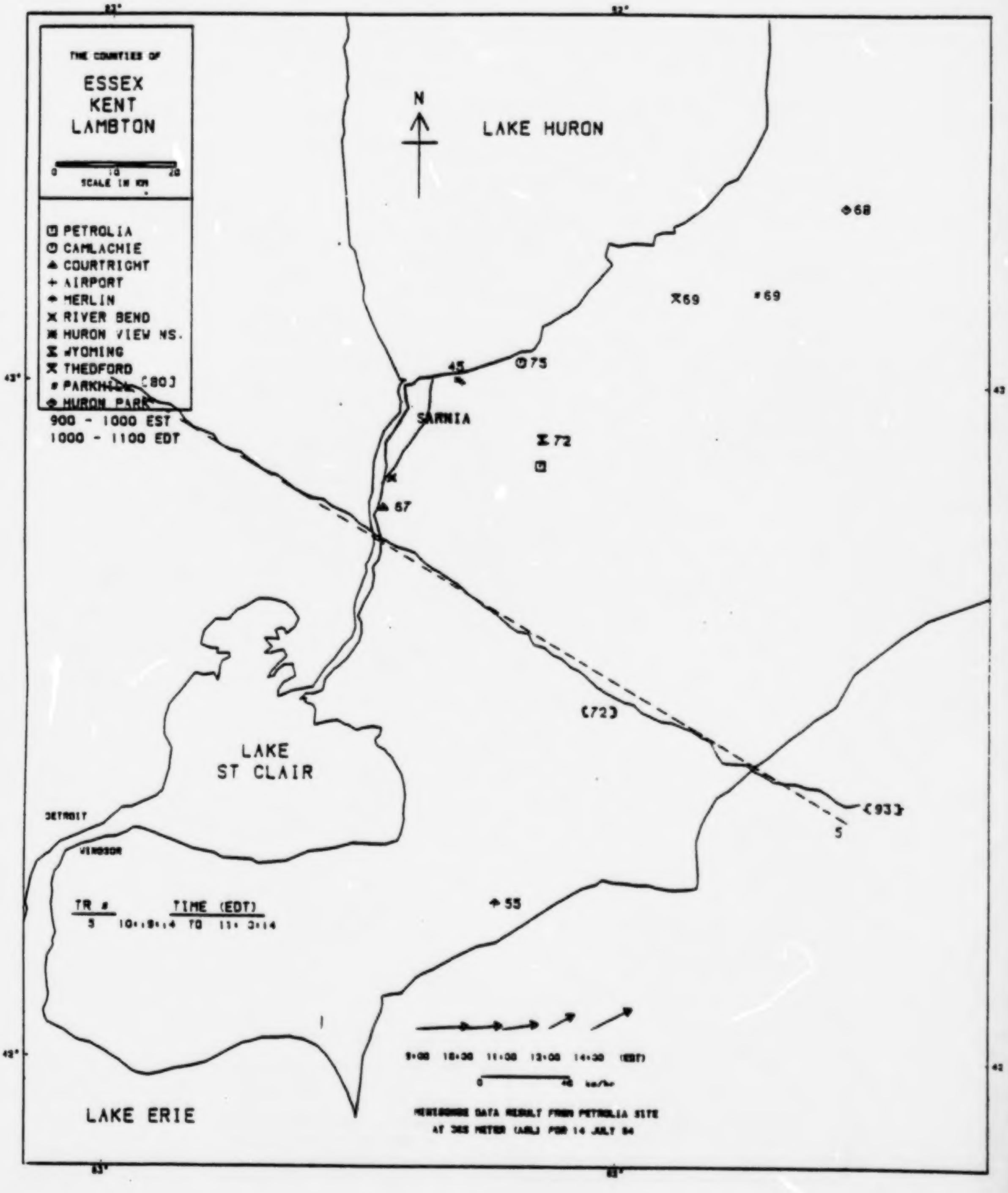

83°
82°
THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
20
SCALE IN KM
□ PETROLIA
○ CAMLACHIE
▲ COURTRIGHT
+ AIRPORT
◆ MERLIN
✕ RIVER BEND
✱ HURON VIEW NS.
⧖ WYOMING
⧗ THEDFORD
# PARKHILL
◇ HURON PARK
900 - 1000 EST
1000 - 1100 EDT
N
LAKE HURON
68
69
69
75
45
SARNIA
72
67
[80]
[72]
[93]
5
43°
42°
LAKE
ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
5
10:19:14 TO 11:03:14
55
9:00
10:30
11:00
13:00
14:30
(EDT)
0
40
km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 305 METER (AGL) FOR 14 JULY 84
LAKE ERIE

Figure 27(c): Ozone Observations in the Sarnia Area on July 14, 10-11 EDT (continued)

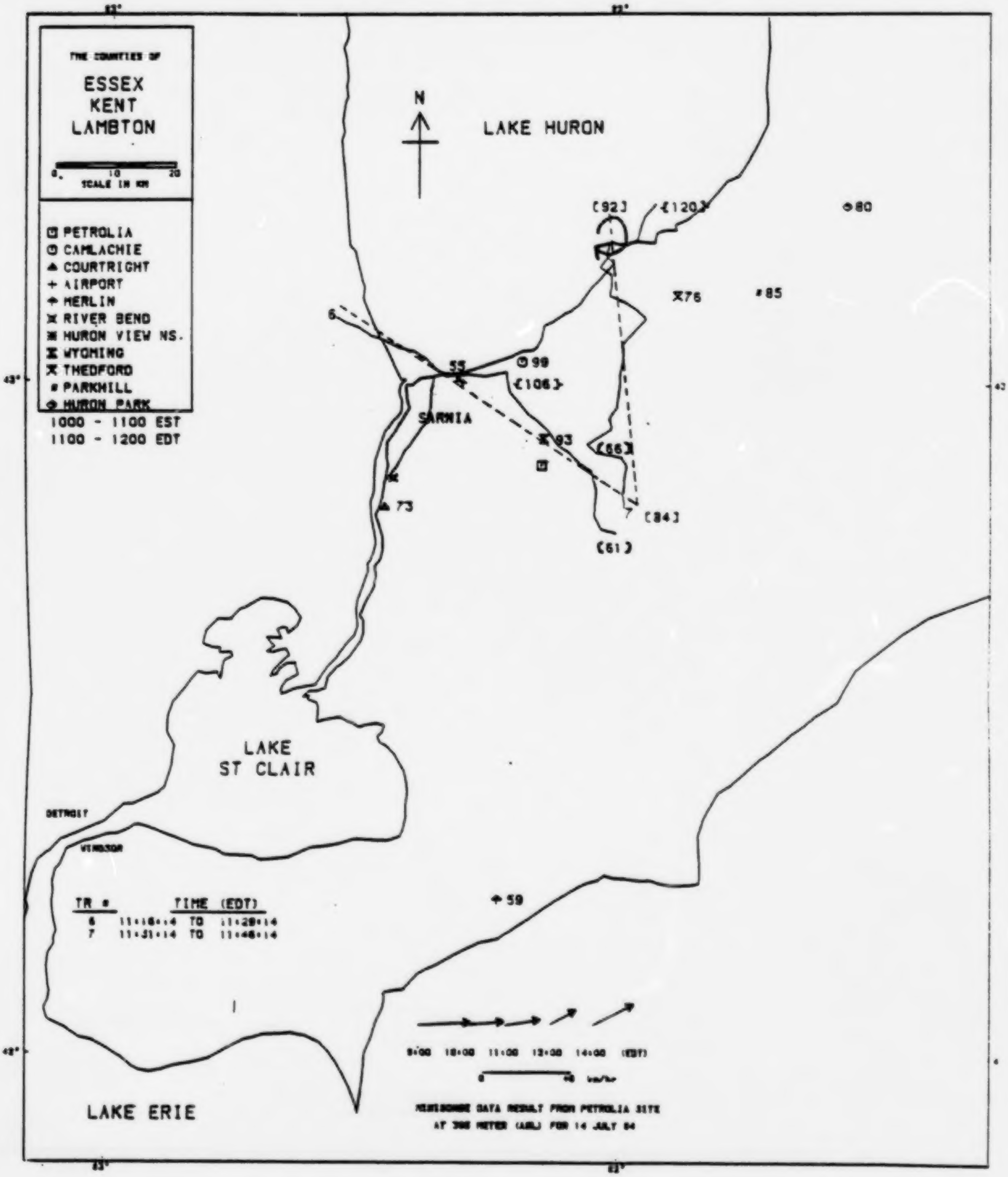

THE COUNTIES OF
ESSEX
KENT
LAMBTON
0 10 20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
1000 - 1100 EST
1100 - 1200 EDT
N
LAKE HURON
[92]
{120}
80
76
85
6
55
99
{106}
SARNIA
93
{66}
7
[84]
[61]
73
LAKE
ST CLAIR
DETROIT
WINDSOR
59
TR #
TIME (EDT)
6 11:16:14 TO 11:29:14
7 11:31:14 TO 11:46:14
9:00 10:00 11:00 12:00 14:00 (EDT)
0 40 km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 300 METER (AGL) FOR 14 JULY 84
LAKE ERIE

Figure 27(d): Ozone Observations in the Sarnia Area on July 14, 11-12 EDT

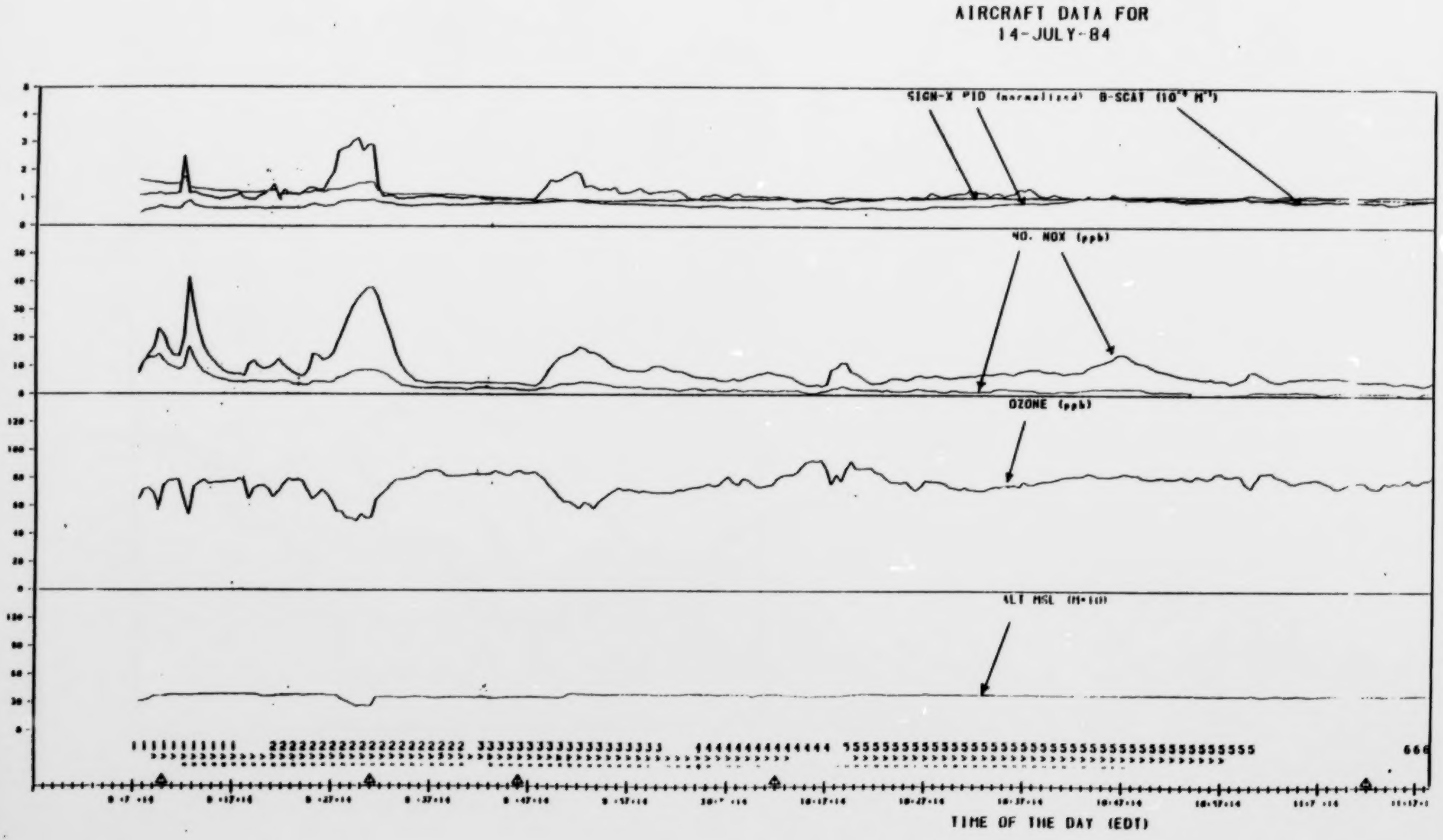


Figure 28: Aircraft Observations on July 14

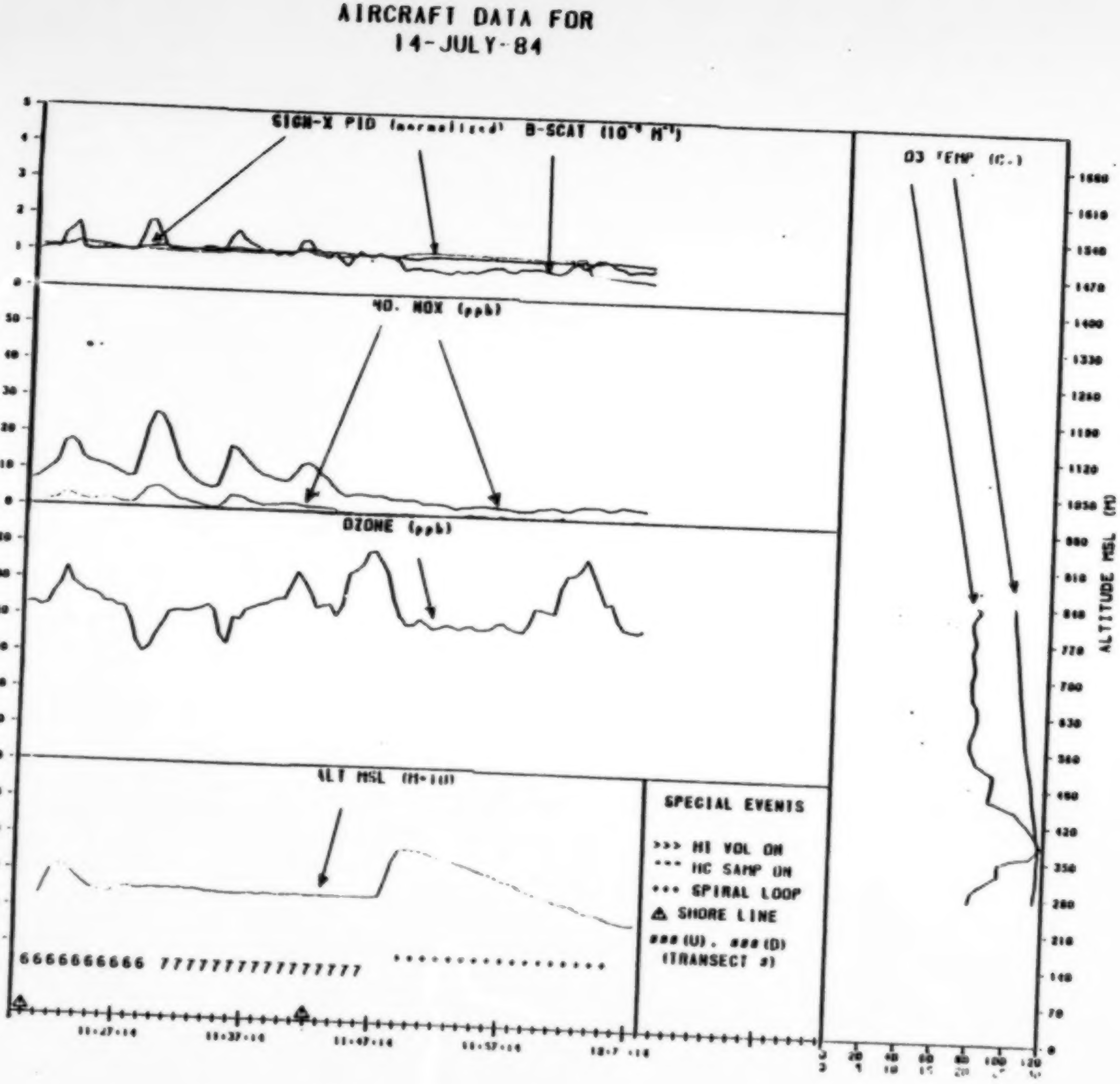


Figure 28: Aircraft Observations on July 14 (continued)

3.9. July 16

On the morning of July 16, a low pressure system was located just to the east of James Bay. A cold front associated with the low extended from Montreal to Memphis and moved southeastward. As a result, the Sarnia region experienced W-NW flows. For the study period (0800 - 1300 EDT), west to northwest winds prevailed with speeds in the 20 - 25 km h^{-1} range. Broken clouds occurred, with temperatures in the low twenties. The hourly solar radiation was variable through the day, but rose to a maximum of 90 - 100 milliwatts cm^{-2} during the period 1200 - 1300 EDT; the surface relative humidity was in the 50 - 60% range. The minisonde data indicate that the mixing depth remained around 400 - 600 m throughout the study period.

Forward trajectories from Sarnia show a southeastward movement. Backward trajectories indicate that air parcels over the Sarnia area had moved from southern Manitoba southeastwards to Sarnia during the previous 48 hours. Both the ground level (Figure 29) and aircraft (Figures 30(a) to (c)) data show low ozone concentrations in the area, less than 40 -45 ppb. The other aircraft measurements (Figure 31) also indicate a clean air mass, in keeping with its past history: sulfate and nitrate values upwind of Sarnia were 4 and 1 ug m^{-3} respectively, the light scattering coefficient was about 0.5×10^{-4} m^{-1}, or less, and sulfur dioxide and nitrogen oxide levels were at instrumental detection limits.

The aircraft traverses were carried out roughly at the mid-point of the mixing layer (about 200 m). Both the upwind and downwind traverses showed little structure in the ozone profiles, with the exception of some scavenging by nitrogen oxides downwind of the generating stations near Courtright (Figures 30(a) - (c)). There was no evidence of any ozone buildups downwind of Sarnia in either the aircraft, or the ground level data. A spiral flown between 200 - 600 m showed that ozone concentrations were essentially uniform within the mixing layer (Figure 31).

The hydrocarbon monitoring results at Camlachie and Courtright show relatively low levels of hydrocarbons (total concentrations of propane and higher hydrocarbons mostly in the 10 - 25 ug m^{-3} range, with alkanes making up the major portion). The aircraft samples show higher levels (with 40 - 50 ug m^{-3} range), with aromatics making up roughly one-half of the total. Since such high levels were observed even on the upwind traverse, contamination of the aircraft samples is suspected.

The ozone precursor levels, as measured at Courtright and Camlachie, were below instrumental detection limits throughout the study period. This result is not surprising, in view of the low levels of hydrocarbons and nitrogen oxides throughout the study area.

A few measurements of oxygen-bearing organic species are available on this day. Formaldehyde levels at Camlachie were found to be in the 0.7 - 2.3 ppb range. Higher aldehydes and ketones (as measured by the TAGA unit at Courtright) were at comparable levels, with the exception of acetone, which was found to be in the 4 -5 ppb range. Relatively high concentrations (4 - 8 ppb) of methanol and propanol were also detected at Courtright.

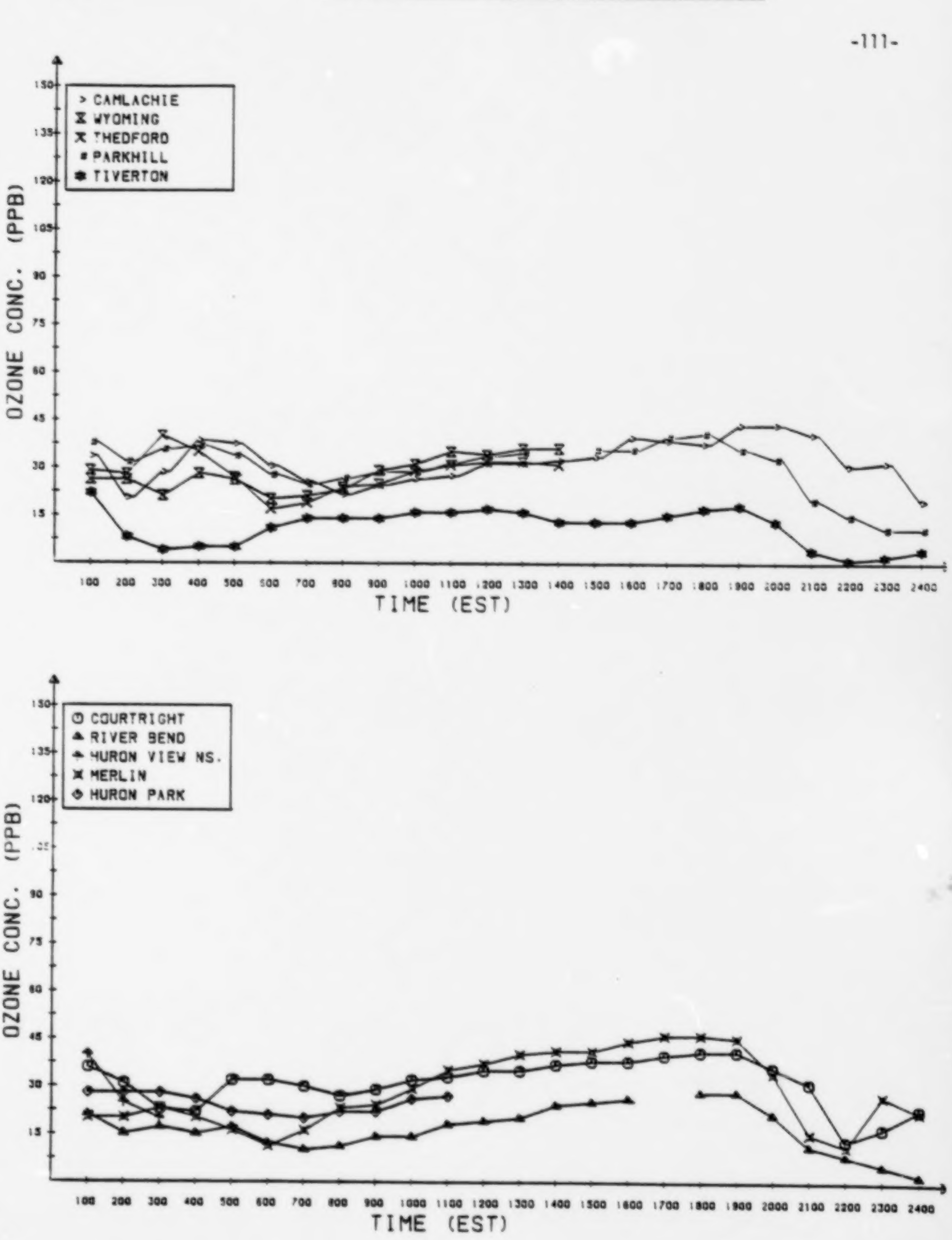


Figure 29: Diurnal Variation of Ozone Concentrations in the Sarnia Area, July 16

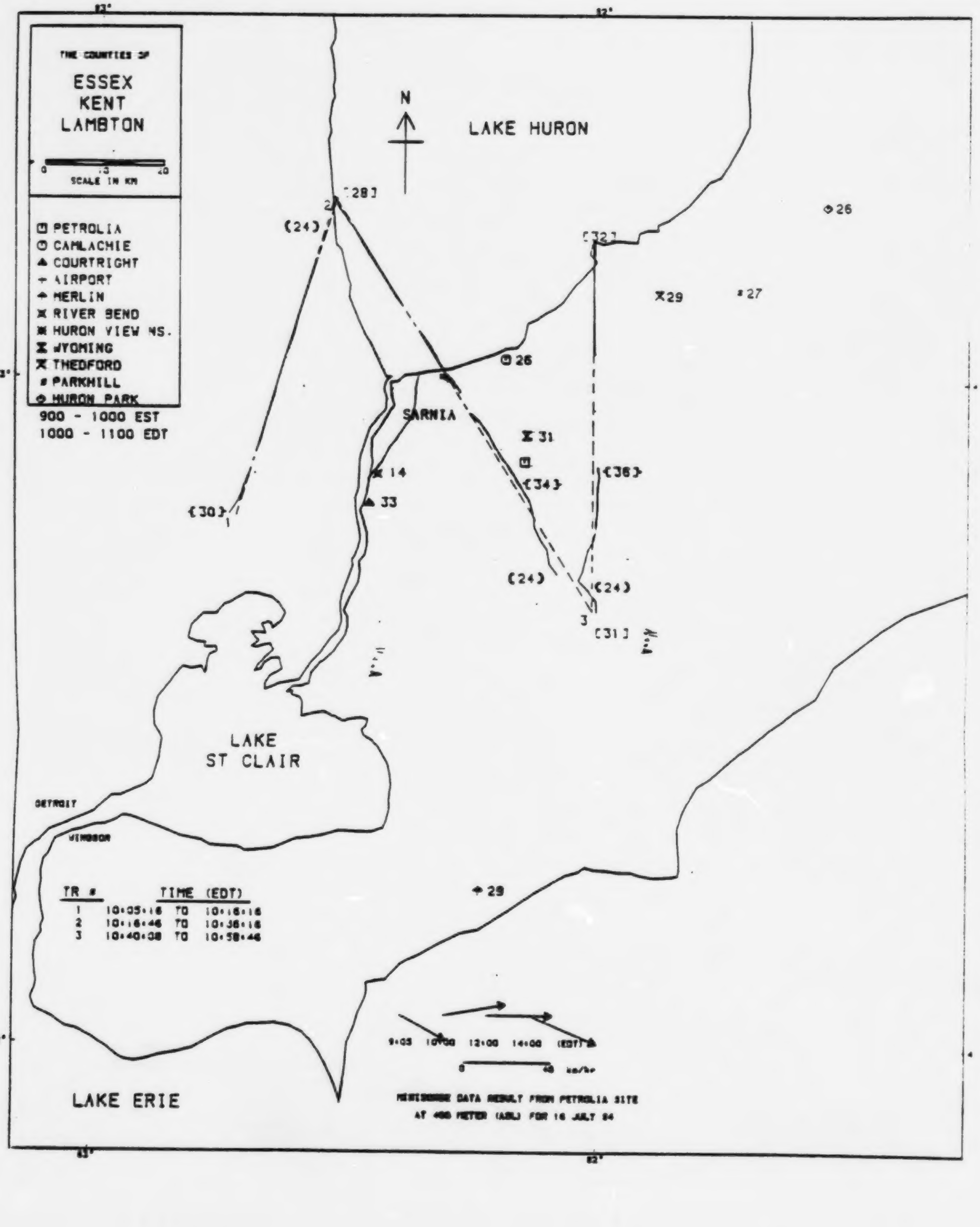

83°
82°
43°
42°
THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
20
40
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW HS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
900 - 1000 EST
1000 - 1100 EDT
N
LAKE HURON
SARNIA
[28]
(24)
2
[32]
26
29
27
26
31
14
33
(30)
1
(34)
(36)
(24)
(24)
3
[31]
LAKE ST CLAIR
DETROIT
WINDSOR
LAKE ERIE
29
TR #
TIME (EDT)
1 10:05:16 TO 10:16:16
2 10:16:46 TO 10:36:16
3 10:40:38 TO 10:58:46
9:05
10:00
12:00
14:00
(EDT)
0
40
km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 400 METER (AGL) FOR 16 JULY 84

Figure 30(a): Ozone Observations in the Sarnia Area on July 16, 10-11 EDT

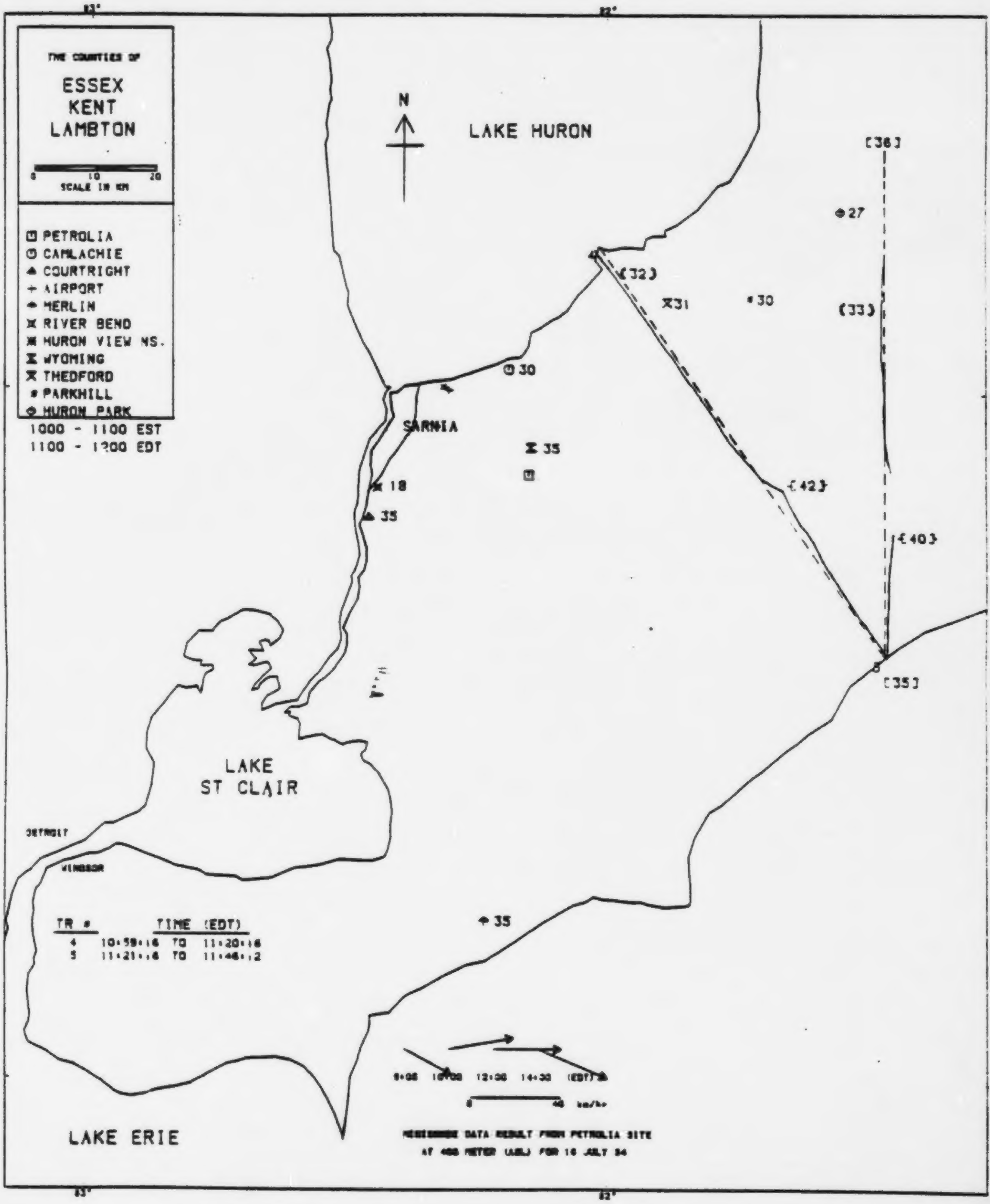

83°
82°
43°
42°
THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
1000 - 1100 EST
1100 - 1200 EDT
N
LAKE HURON
SARNIA
30
35
18
35
[32]
31
30
27
[38]
[33]
[42]
[40]
[35]
LAKE ST CLAIR
DETROIT
WINDSOR
35
TR #
TIME (EDT)
4 10:59:16 TO 11:20:16
5 11:21:16 TO 11:46:12
9:00
10:00
12:00
14:00
(EDT)
0
40
km/hr
RAWINSONDE DATA RESULT FROM PETROLIA SITE
AT 400 METER (AGL) FOR 16 JULY 84
LAKE ERIE

Figure 30(b): Ozone Observations in the Sarnia Area on July 16, 11-12 EDT

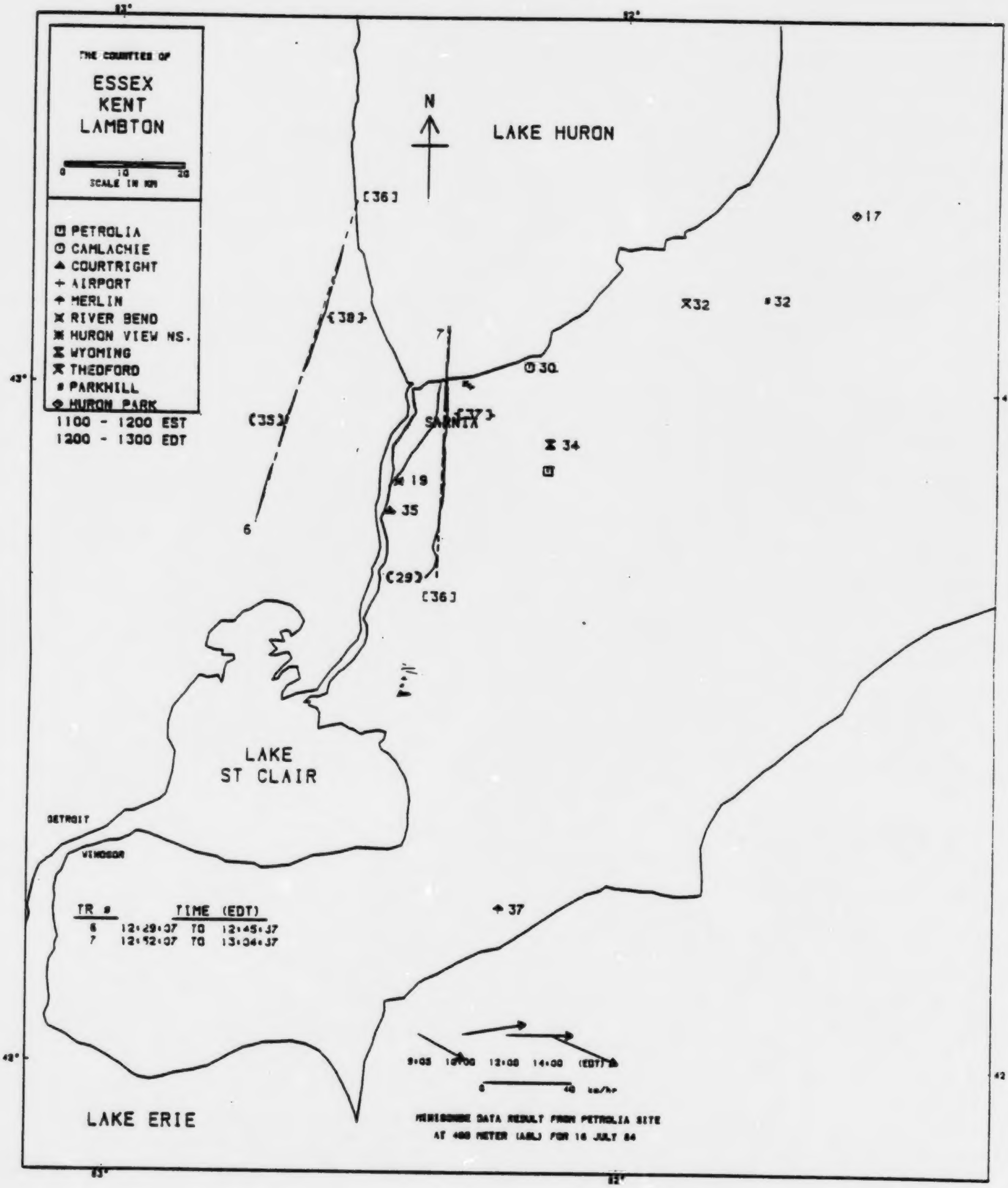

83°
82°
43°
43
42°
42
THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
20
SCALE IN KM
▣ PETROLIA
◎ CAMLACHIE
▲ COURTRIGHT
+ AIRPORT
✦ MERLIN
✕ RIVER BEND
✱ HURON VIEW NS.
⧗ WYOMING
⊼ THEDFORD
▪ PARKHILL
◈ HURON PARK
1100 - 1200 EST
1200 - 1300 EDT
N
LAKE HURON
[36]
[38]
[35]
6
7
SARNIA
[37]
◎ 30
⧗ 34
▣
✱ 19
▲ 35
[29]
[36]
◈ 17
⊼32
▪32
LAKE
ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
6 12:29:37 TO 12:45:37
7 12:52:37 TO 13:34:37
✦ 37
9:00 10:00 12:00 14:00 (EDT)
0 40 km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 400 METER (AGL) FOR 16 JULY 84
LAKE ERIE

Figure 30(c): Ozone Observations in the Sarnia Area on July 16, 12-13 EDT

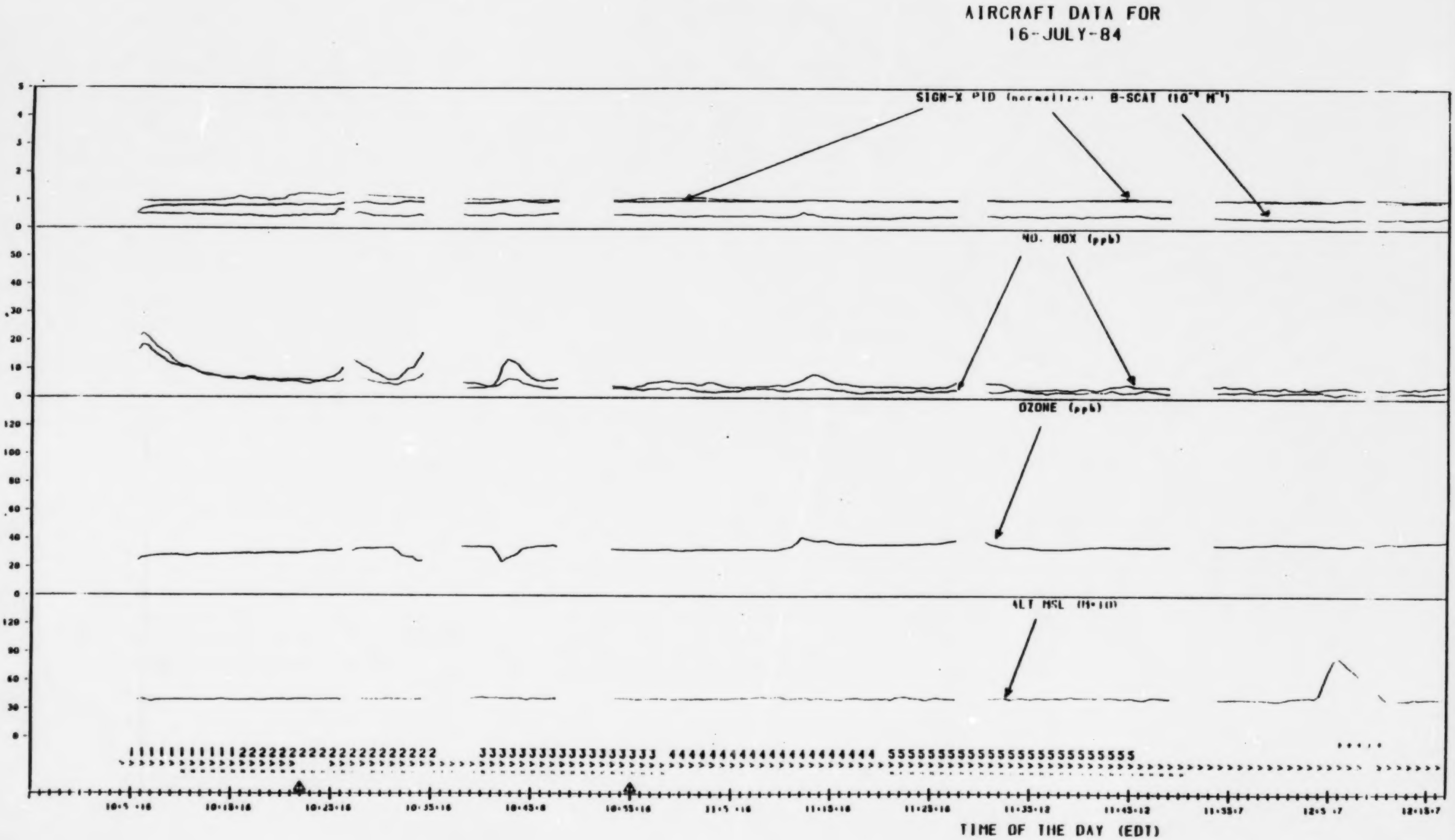


Figure 31: Aircraft Observations on July 16

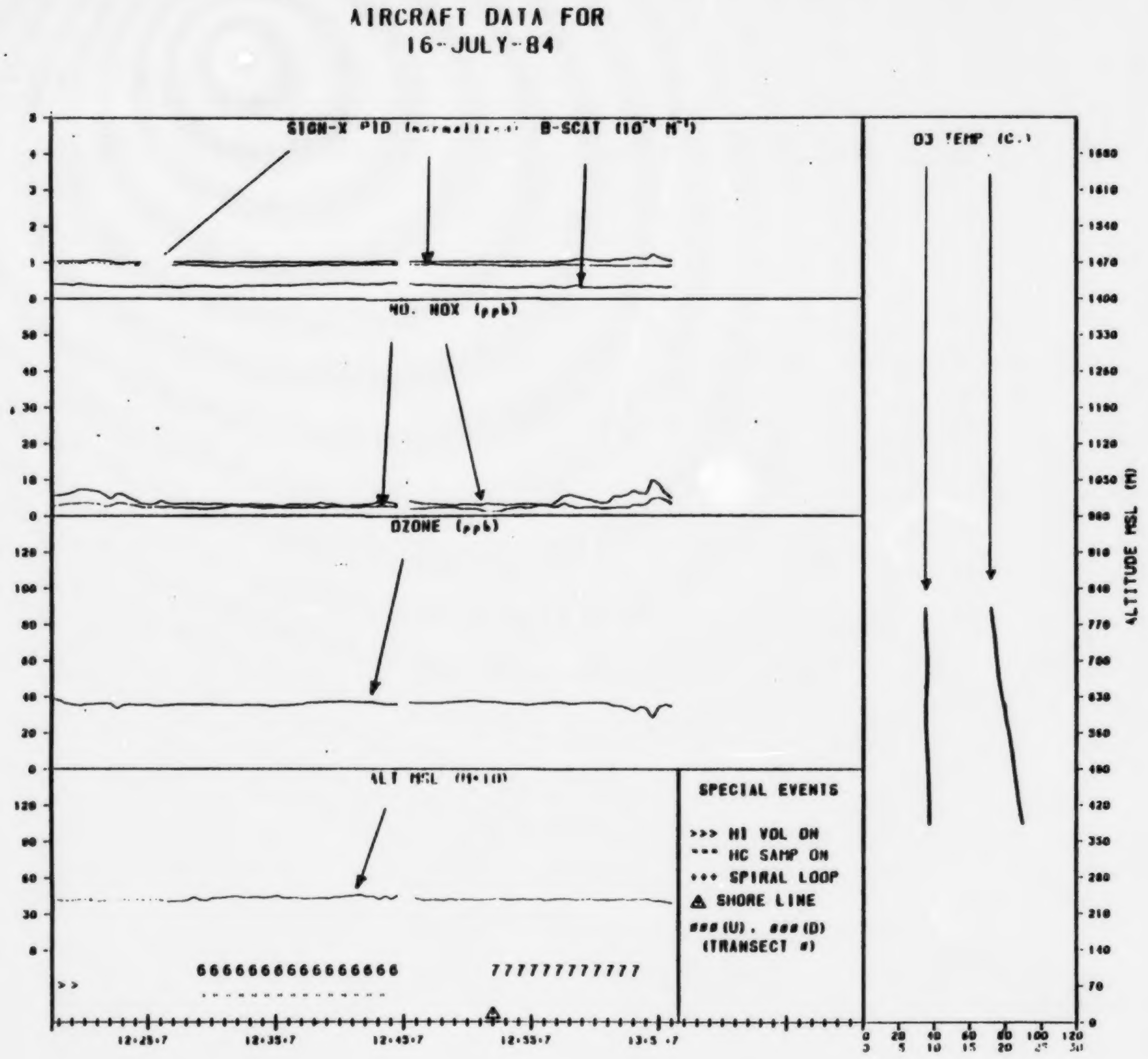


Figure 31: Aircraft Observations on July 16 (continued)

3.10. July 17

On July 17, a low pressure system was moving slowly southeastwards across the Upper Great Lakes. The Sarnia region, in the warm sector of the frontal system associated with the low, experienced southwesterly flows, with wind speeds in the 15 - 20 km h^{-1} range during the study period (0800 - 1100 EDT). Skies were overcast with temperatures in the low twenties. At the time of the aircraft flights, the hourly average solar radiation was about 30 milliwatts cm^{-2}, and the surface relative humidity was in the 60 - 70% range. At the start of the flight, the atmosphere was stable: towards the end, the depth of the mixing layer was at about 500 m. Forward trajectories from Sarnia show a northeastward movement. Backward trajectories indicate a movement from northern Minnesota southeastward to lower Lake Michigan and then northeastward to Sarnia during the previous 48 hours.

The aircraft sampling program consisted of a number of traverses upwind, over the Sarnia area, and downwind (between 0900 and 1000 EDT), at an altitude of about 220 m, followed by two spirals between 250 and 1000 m - one over Kettle Point, on the shore of Lake Huron, and the other over Sarnia.

During the period of the flight, ozone concentrations in the area were low -generally less than 40 ppb (Figures 32 and 33). The aircraft data show a considerable amount of structure in the horizontal ozone profiles, mainly due to "dips" attributable to scavenging by NO_x plumes, both upwind and downwind of Sarnia (see Figure 34). A notable feature of the aircraft data is the relatively high NO_x levels which were observed during almost all the traverses, with concentrations in the 20 - 40 ppb range, the NO_x being mainly in the form of NO_2. There seem to be several broad upwind plumes, probably from the Detroit area, or generating stations on the U.S. side of the border, north of Lake St. Clair, and traverses 2 and 6 also show a plume possibly originating from the generating station at Courtright. There is no clear evidence in the data -either airborne or ground-level-of any ozone buildups from the Windsor/Detroit, or the Sarnia areas. The spirals (Figure 34) indicated that ozone levels above the mixing layer were higher than those below, by about 20 ppb (this is probably due to the fact that NO_x concentrations above the mixing layer were low, at about 5 ppb).

During the aircraft sampling period, (9 - 11 hours) hydrocarbon concentrations were quite high. The table below summarizes these observations:

Location	Time EDT	Total HC (C_{3+})ug m^{-3}	Alkanes %	Alkenes %	Aromatics %
Courtright	0910-1010	99	66	0.6	26
(upwind)	1010-1110	60	63	5	21
Camlachie	0858-0958	104	74	0.6	19
(downwind)	0958-1058	89	62	0.4	33
Airplane					
(upwind)	0902-0920	53	76	0.7	22
(downwind)	0929-0944	46	59	0	38

Camlachie was approximately downwind of Sarnia, while Courtright was upwind. Although the former site had somewhat higher total hydrocarbon levels than the latter, the composition of the upwind and downwind hydrocarbon mixtures is similar, and also roughly resembles that sampled in the aircraft, a rather large fraction being attributable to alkanes, benzene and alkyl benzene.

In view of the relatively high concentrations of ozone precursors (NO_x and hydrocarbons) in the area, it was interesting to examine the ozone precursors monitor results at Camlachie and Courtright. Values were in the 11 - 20 ppb range, somewhat higher than average for the overall study period.

During the morning, the tunable diode laser at Camlachie recorded formaldehyde levels in the 1 - 2 ppb range. The TAGA unit at Courtright found other oxygenated organic compounds to be at levels of 1 ppb or less, except for acetone and methanol, which were at about 2 ppb.

No sulfate or nitrate samples were taken during this flight. Nephelometer readings ($b_{scat} \times 10^4$) were in the 0.5 - 1.0 m^{-1} range.

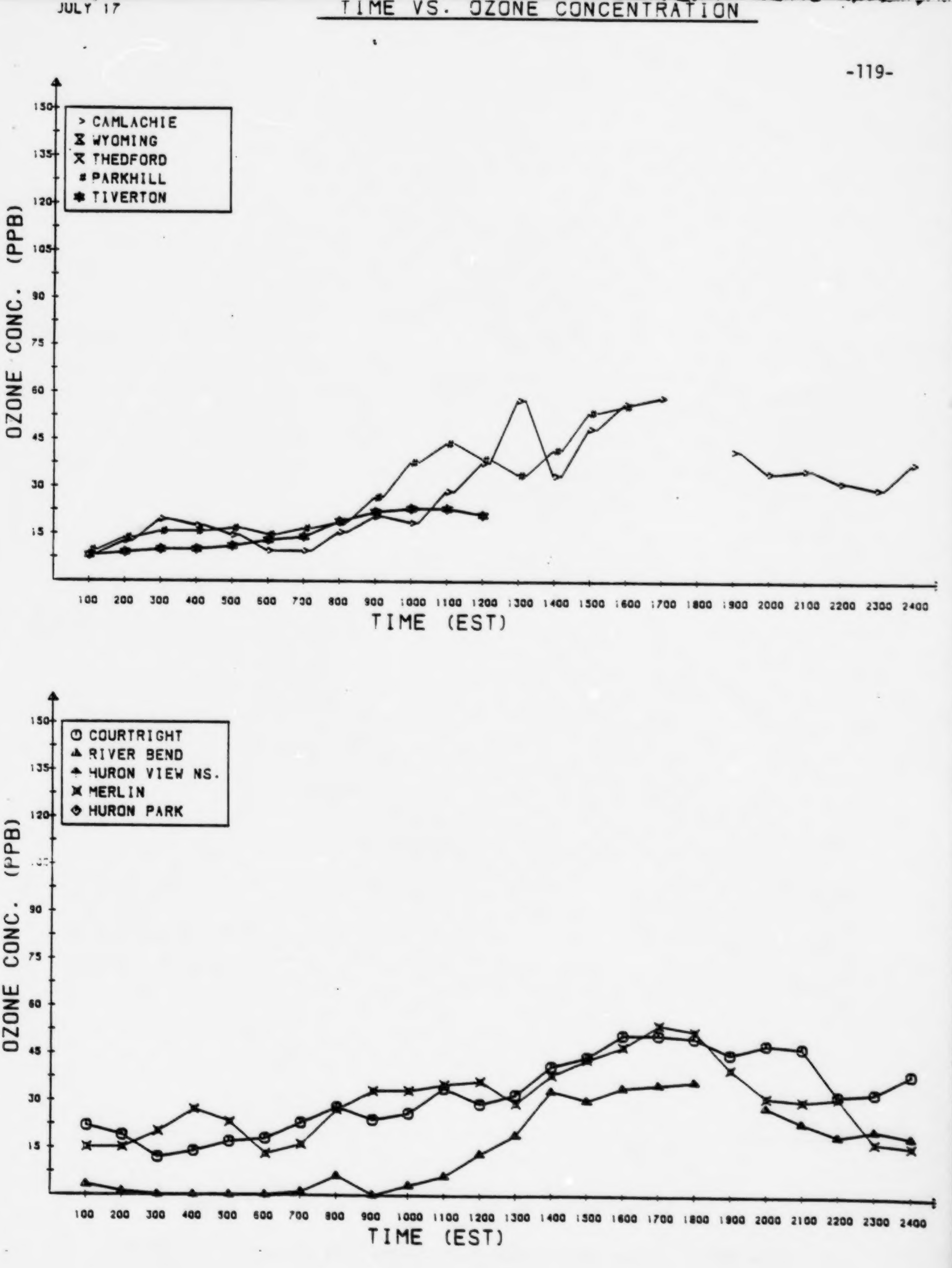


Figure 32: Diurnal Variation of Ozone Concentrations in the Sarnia Area, July 17

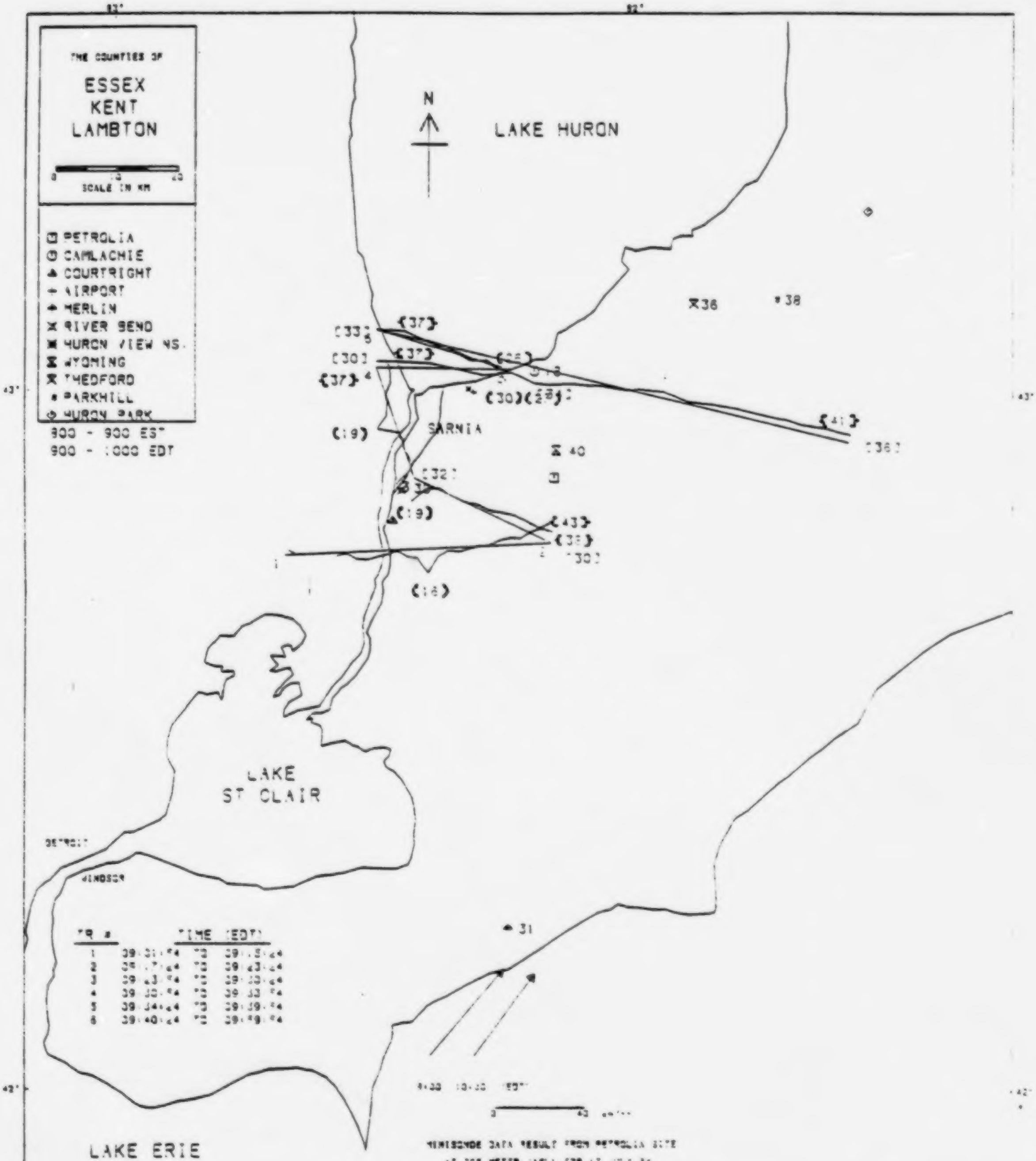

THE COUNTIES OF
ESSEX
KENT
LAMBTON
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW HS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
800 - 900 EST
900 - 1000 EDT
N
LAKE HURON
SARNIA
LAKE ST CLAIR
LAKE ERIE
DETROIT
WINDSOR
36
38
40
31
{37}
{37}
{37}
{19}
{19}
{43}
{16}
{41}
[33]
[30]
[32]
[36]
[30]
TR #
TIME (EDT)

Figure 33(a): Ozone Observations in the Sarnia Area on July 17, 9-10 EDT

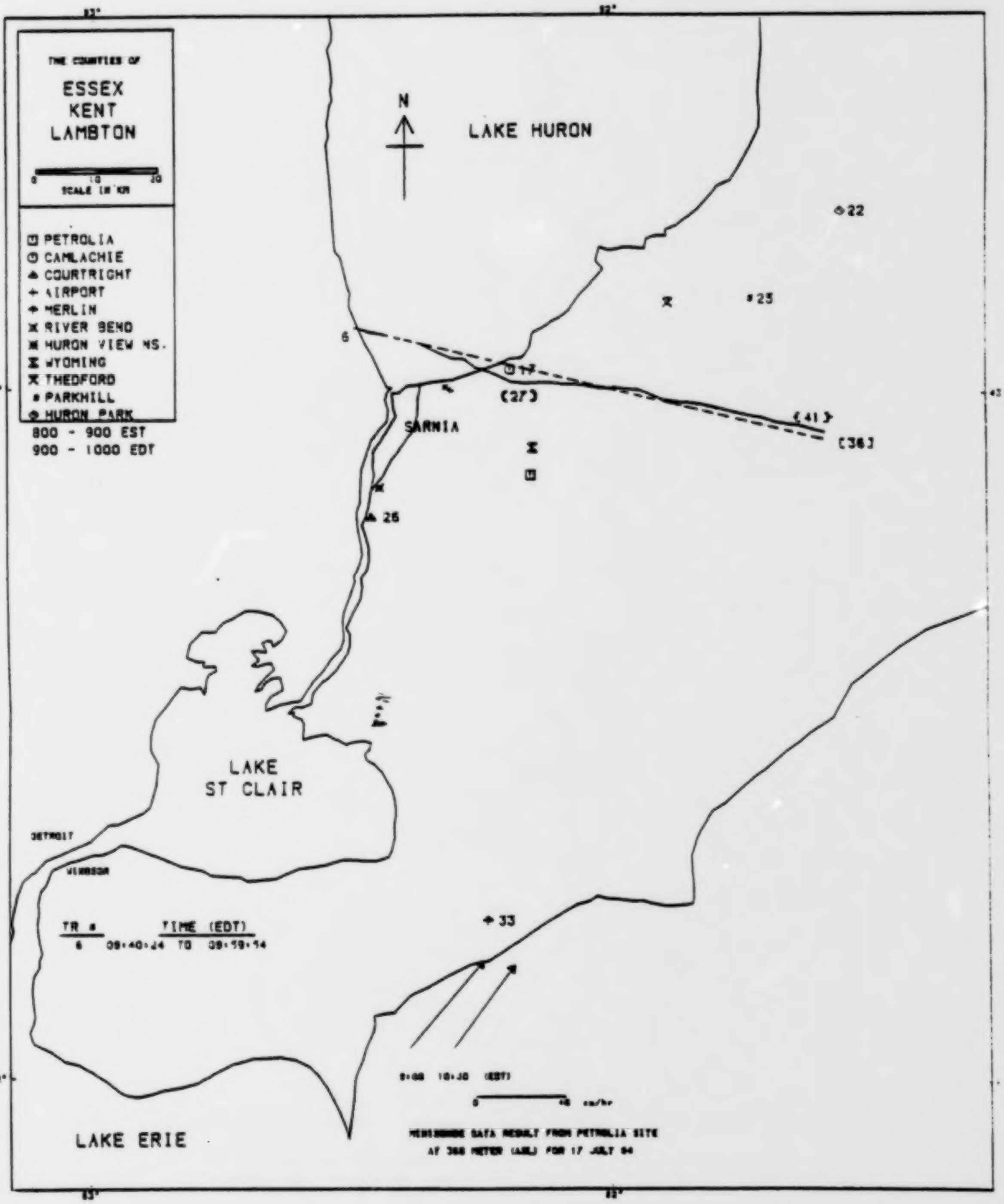

83°
82°
THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
800 - 900 EST
900 - 1000 EDT
N
LAKE HURON
22
25
6
17
(27)
(41)
(36)
43°
SARNIA
26
LAKE ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
6
09:40:24 TO 09:59:54
33
42°
9:00
10:30
(EDT)
0
LAKE ERIE
PETROLIA SITE
FOR 17 JULY 84

Figure 33(b): Ozone Observations in the Sarnia Area on July 17, 9-10 EDT (continued).

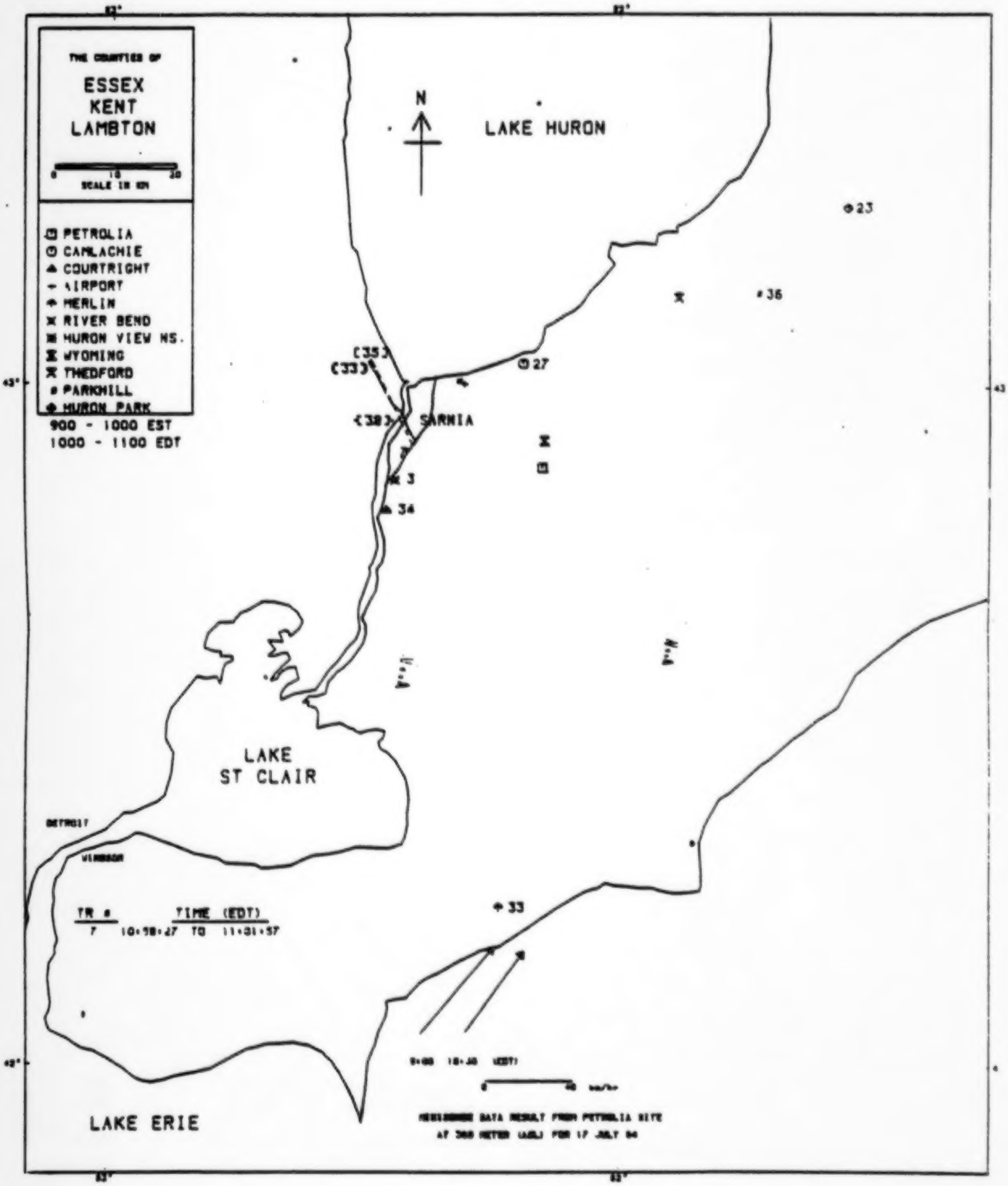

THE COUNTIES OF
ESSEX
KENT
LAMBTON
0 10 20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW HS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
900 - 1000 EST
1000 - 1100 EDT
N
LAKE HURON
23
36
(35)
(33)
27
(38)
SARNIA
3
34
LAKE ST CLAIR
DETROIT
WINDSOR
TR #
7
TIME (EDT)
10:58:27 TO 11:01:57
33
9:00 10:30 (EDT)
0 40 km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 300 METER (AGL) FOR 17 JULY 84
LAKE ERIE
43°
42°
83°
82°

Figure 33(c): Ozone Observations in the Sarnia Area on July 17, 10-11 EDT

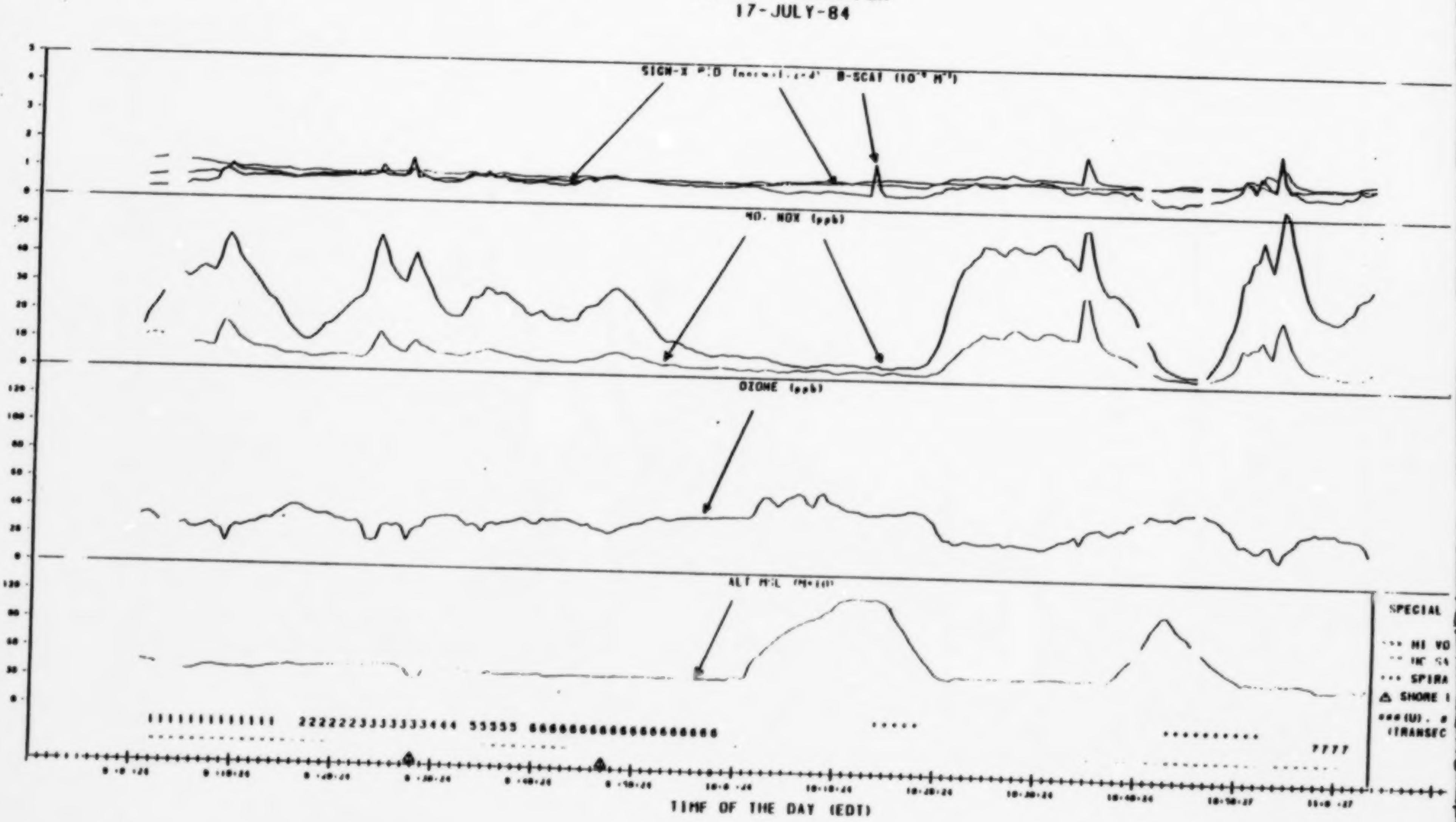


Figure 34: Aircraft Observations on July 17

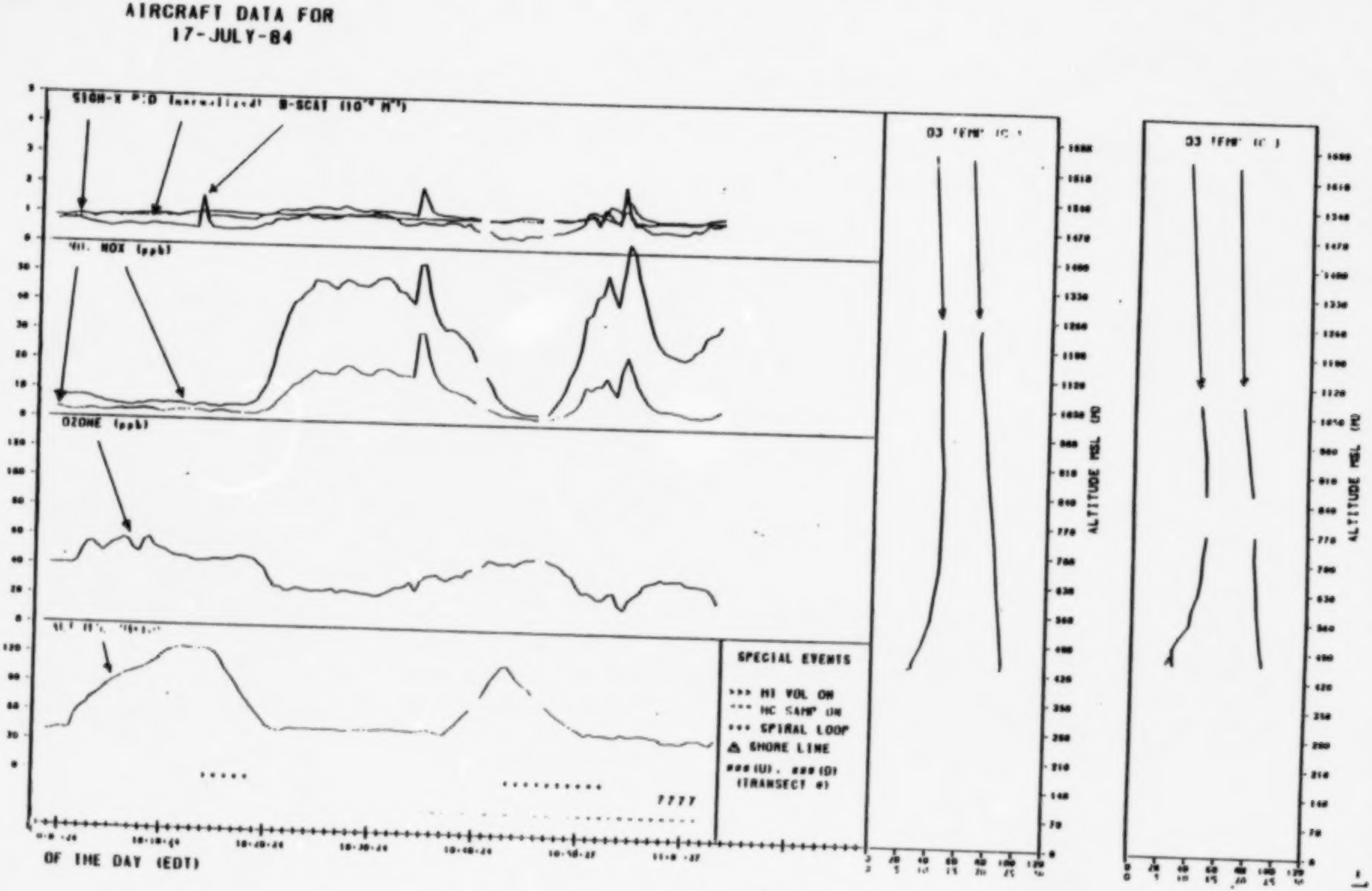


Figure 34: Aircraft Observations on July 17 (continued)

3.11. July 18

The low pressure system which moved across the Upper Great Lakes on July 17 continued to track slowly eastward into southwestern Quebec on July 18, and dissipated there. The cold front from this low extended southwestwards through Lake Ontario. As a result, the Sarnia region experienced west-northwest flows behind the cold front. For the study period, winds were predominantly northwest at 20 km h^{-1}. Cloudy, overcast conditions occurred with some showers, and temperatures in the upper teens. At the time of the aircraft flights (1100 - 1300 EDT), the hourly average solar radiation was in the 60 - 80 mw cm^{-2} range, and the relative humidity was 60 - 80 %. Based on minisonde data at Camlachie and Petrolia during the period 0800 - 1100 EDT, the initial mixing depth was around 400 m. The depth through the morning remained below 800 m.

Forward trajectories from Sarnia show a southeastward movement. Backward trajectories (during the previous 48 hours) indicate a path from Central Minnesota eastward through Lake Michigan and then southeastward to Sarnia. These "clean" air parcel origins are confirmed by the low ozone levels observed throughout the area on July 18th (Figure 35) - typically less than 45 ppb - and the good visibility (see Figure 37 - b_{scat}, as measured by the nephelometer, being approximately 0.5×10^{-4} m^{-1}), although a hivol sample taken upwind of Sarnia showed surprisingly high sulfate levels at 17 ug m^{-3} (nitrates were found to be 1.8 ug m^{-3}).

The aircraft traverses were carried out at an altitude of about 240 m, upwind and downwind of Sarnia (Figures 36(a) to (c)), with the exception of traverses 2 and 3, which were flown between the same end points as traverse 1, but approximately 80 m below and above traverse 1 respectively. Very little variation in ozone levels was observed during the sampling period - either vertically or horizontally. The aircraft and ground level data show no evidence of any ozone plume, and upwind (traverse 6) and downwind concentrations are seen to be similar.

Hydrocarbon and NO_x levels were found to be low throughout the study area during the morning of July 18 (at the time of the aircraft flights, concentrations of propane and higher hydrocarbons were no greater than 20 ug m^{-3}, consisting largely of alkanes and aromatics, while NO_x levels were generally below 10 ppb). Ozone precursor monitor measurements were below detection limits. No formaldehyde or hydrogen peroxide data are available from the tunable diode laser at Camlachie. The TAGA system at Courtright indicated most other oxygenated organics (aldehydes, ketones, acetates and alcohols) to be below instrumental detection limits.

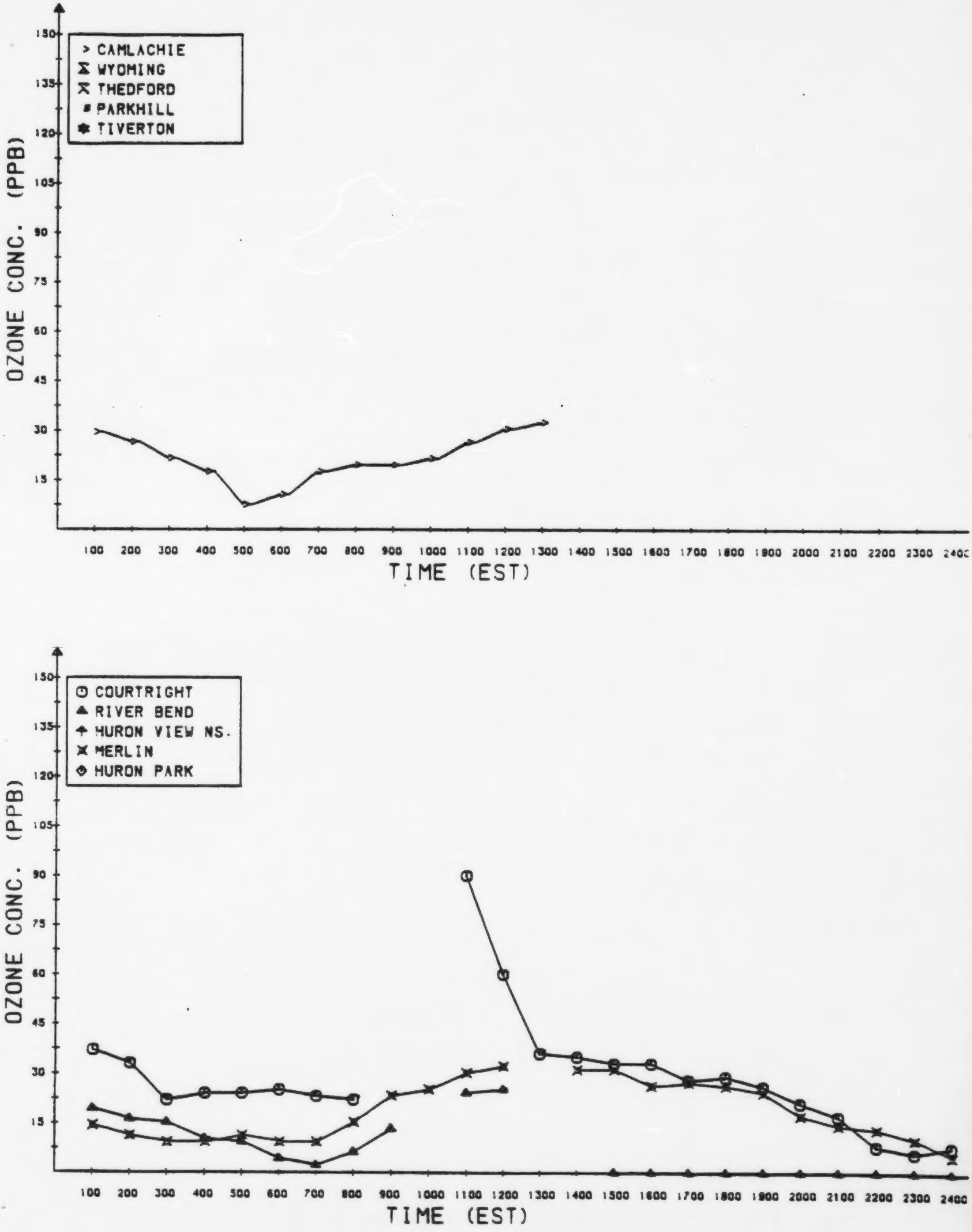


Figure 35: Diurnal Variation of Ozone Concentrations in the Sarnia Area, July 18

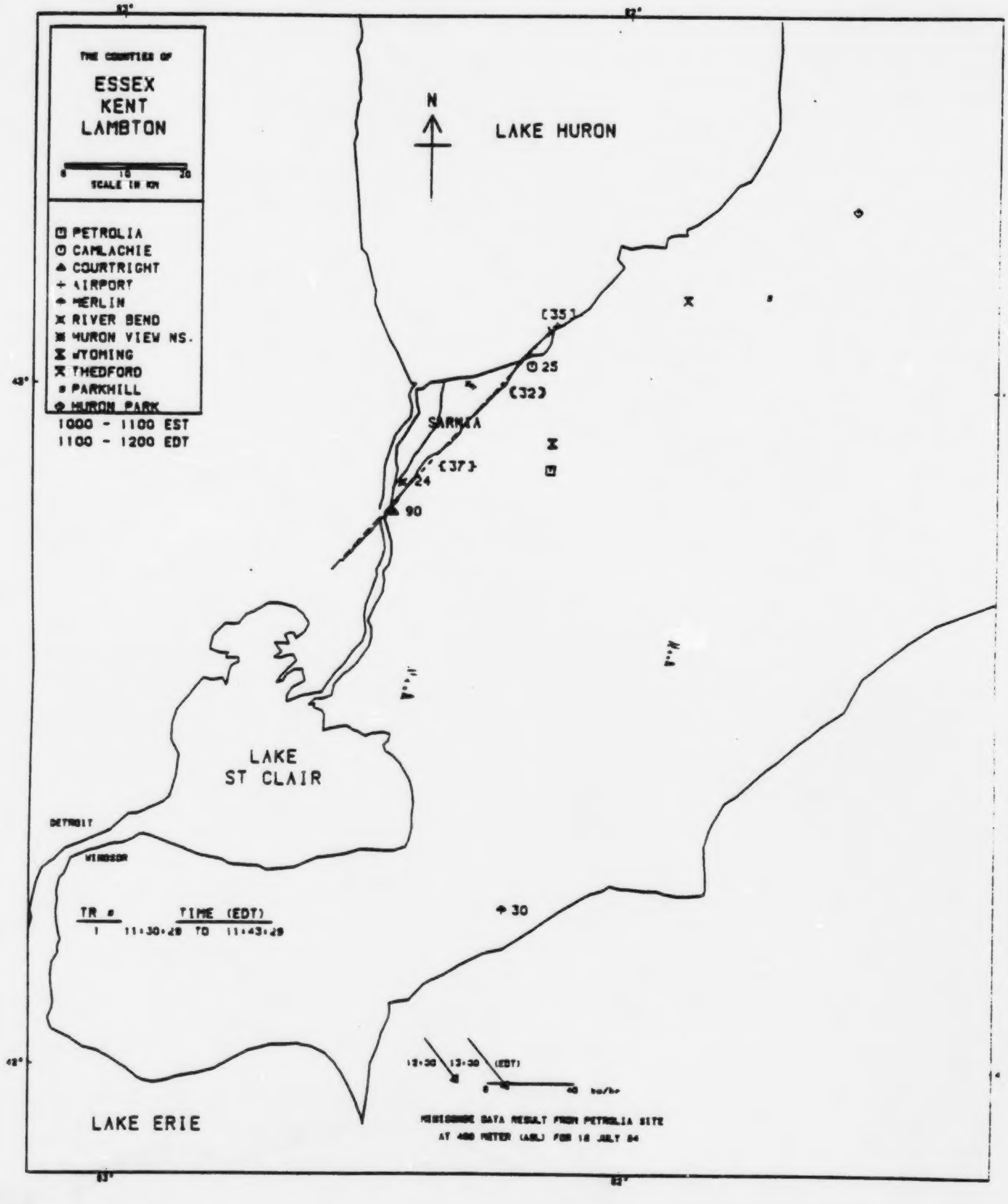

83°
82°
THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
20
SCALE IN KM
▣ PETROLIA
○ CAMLACHIE
▲ COURTRIGHT
+ AIRPORT
♦ MERLIN
✕ RIVER BEND
✱ HURON VIEW NS.
⧗ WYOMING
⌆ THEDFORD
• PARKHILL
◇ HURON PARK
1000 - 1100 EST
1100 - 1200 EDT
N
LAKE HURON
[35]
25
[32]
SARNIA
[37]
24
90
43°
42°
LAKE
ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
1
11:30:29 TO 11:43:29
30
12:30
13:30
(EDT)
0
40
km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 400 METER (ASL) FOR 18 JULY 84
LAKE ERIE

Figure 36(a): Ozone Observations in the Sarnia Area on July 18, 11-12 EDT

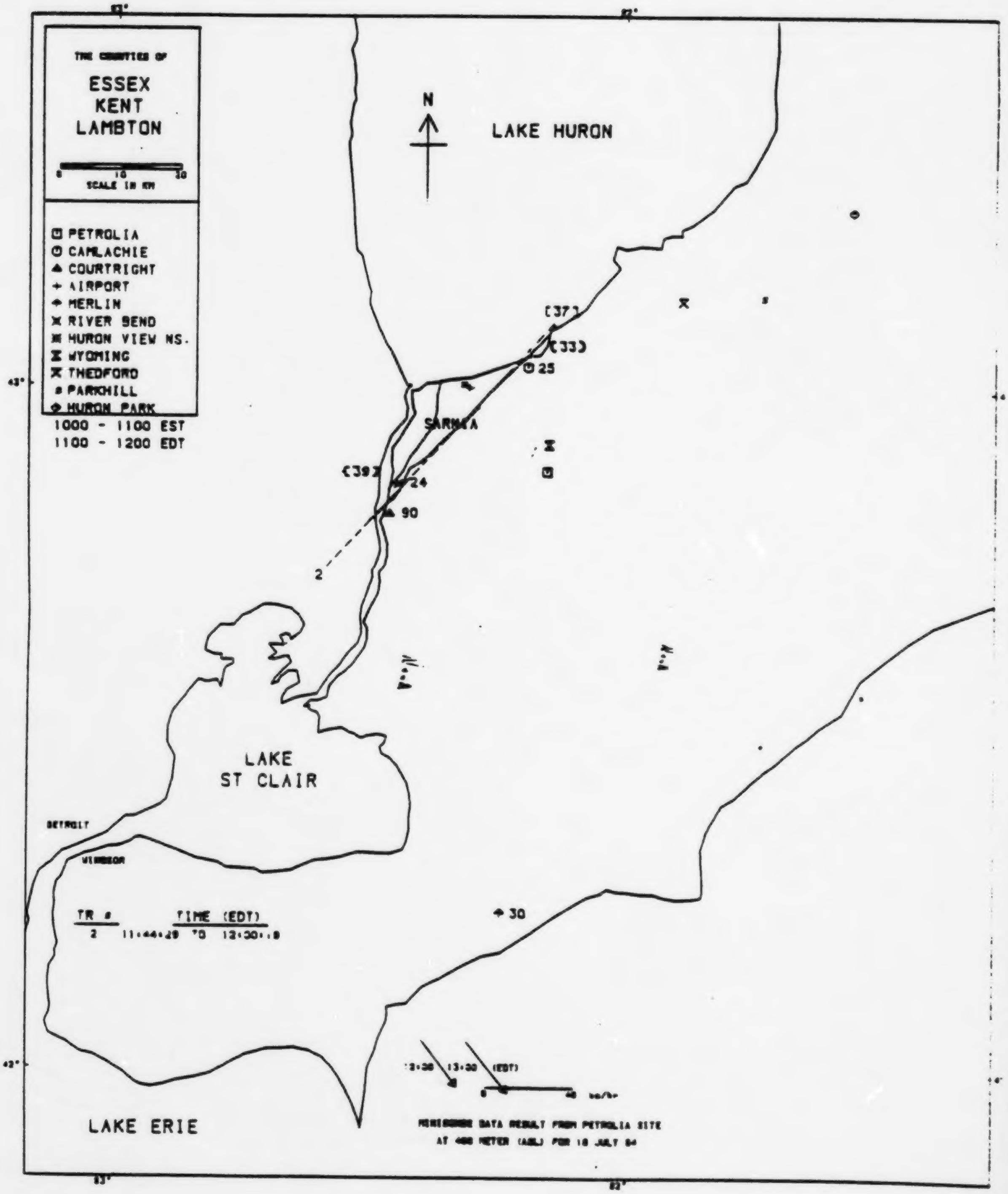

THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
1000 - 1100 EST
1100 - 1200 EDT
N
LAKE HURON
[37]
[33]
25
SARNIA
[39]
24
90
2
LAKE ST CLAIR
DETROIT
WINDSOR
TR #
TIME (EDT)
2
11:44:29 TO 12:30:18
30
13:30
(EDT)
0
40
km/hr
MINISONDE DATA RESULT FROM PETROLIA SITE
AT 400 METER (AGL) FOR 18 JULY 84
LAKE ERIE
83°
82°
43°
42°

Figure 36(b): Ozone Observations in the Sarnia Area on July 18, 11-12 EDT (continued)

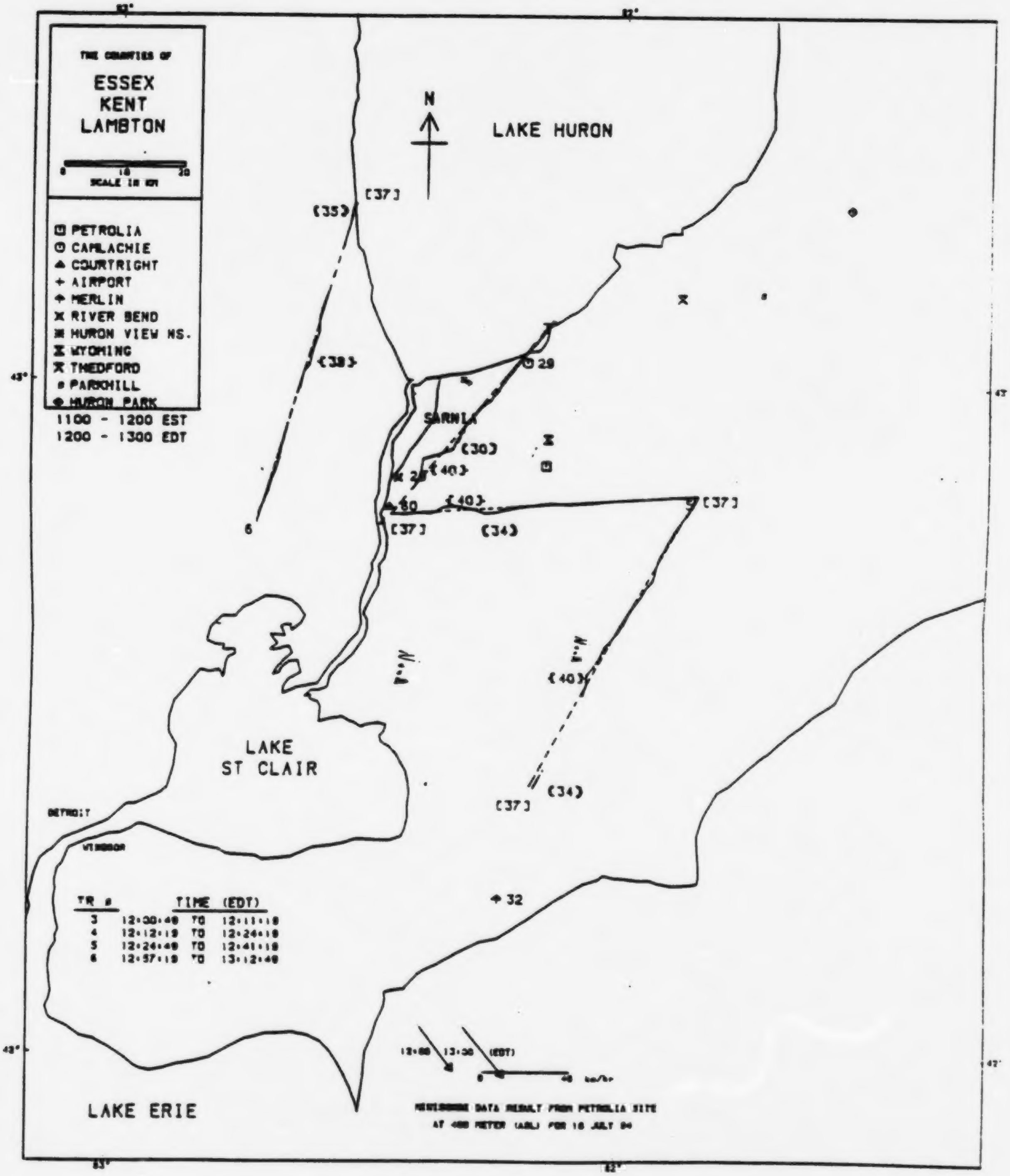

THE COUNTIES OF
ESSEX
KENT
LAMBTON
0
10
20
SCALE IN KM
PETROLIA
CAMLACHIE
COURTRIGHT
AIRPORT
MERLIN
RIVER BEND
HURON VIEW NS.
WYOMING
THEDFORD
PARKHILL
HURON PARK
1100 - 1200 EST
1200 - 1300 EDT
N
LAKE HURON
LAKE ST CLAIR
LAKE ERIE
SARNIA
DETROIT
WINDSOR
[37]
{35}
{38}
29
{30}
{40}
{40}
[37]
[37]
{34}
{40}
{34}
[37]
6
32
TR #
TIME (EDT)
3 12:30:49 TO 12:11:19
4 12:12:19 TO 12:24:19
5 12:24:49 TO 12:41:19
6 12:57:19 TO 13:12:49
13:00
13:30
(EDT)
0
40
km/hr
DATA RESULT FROM PETROLIA SITE
FOR 18 JULY 84
83°
82°
43°

Figure 36(c): Ozone Observations in the Sarnia Area on July 18, 12-13 EDT

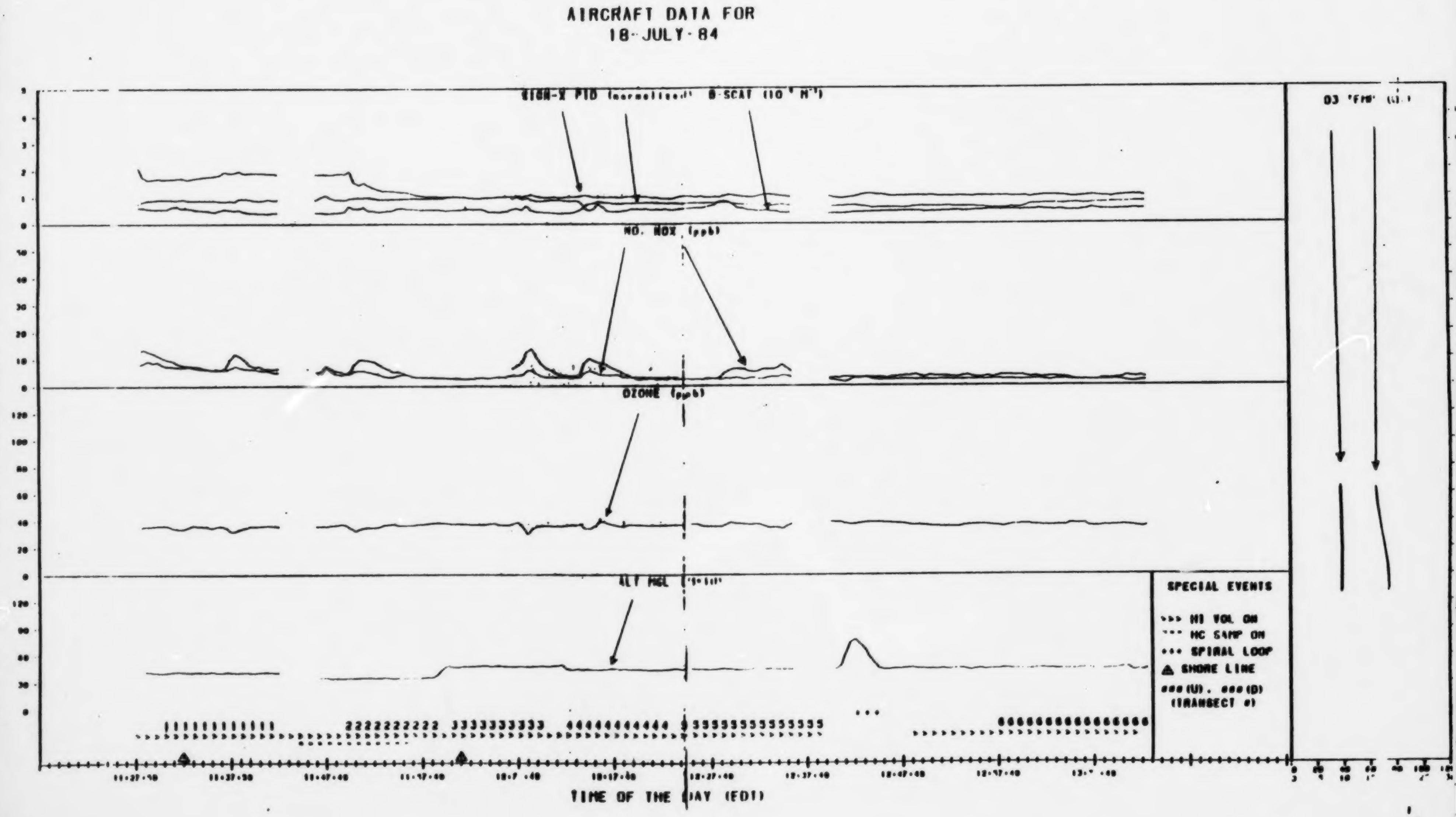


Figure 37: Aircraft Observations on July 18

cing the discussion of the results, a few comments
orological representativeness of the study period may be in
der (see MOE Report ARB-023-85-AQM). A comparison of the synoptic weather situation at 0700 EST for each day during the study period with the same 24-day period in the years 1976-1983 showed a more frequent number of days with "front of the high" northerly flow and cyclonic activity than the other years, and a less frequent number of days with a lack of synoptic pattern (i.e. small pressure gradient over the eastern Great Lakes not associated with any specific weather system). Based on previous work (Heidorn and Yap, 1984), such a situation leads us to expect relatively low average ozone levels during this specific period taken as a whole, when compared to the long-term data. On no occasion was there a period of several consecutive days that was conducive to establishing a pattern of extensive elevated ozone concentrations (i.e. when a run of synoptic "back-of-the high pressure system", or "centre-of-the-high/no-gradient", days occurs). The above facts introduce some uncertainty when generalizing the results of this study to the long-term assessment of the impact of Sarnia emissions versus long-range transport on oxidant levels in southern Ontario. Nevertheless, a number of interesting observations can be made. The reader is referred to Table 4, which summarizes the observations on ozone and ozone precursor levels in the area, as well as the concurrent meteorological conditions, during the study period.

4.1 Frequency of Occurrence of a Sarnia Impact

An examination of Table 4 indicates that on four out of eleven days when aircraft flights were carried out, there was evidence for ozone buildups in the study area due to Sarnia emissions, either as downwind "plumes" (June 28, July 13), or "patches" of elevated ozone levels on the calmer days (July 8 and 14). On these occasions, maximum ozone buildups (over and above "background" levels) of about 20-40 ppb were observed. In agreement with the recently-published observations of Kelly et al. (1985) regarding the impact of Detroit on ozone concentrations in nearby areas in Michigan and Ontario, the plume maxima occurred at some istance from the Sarnia industrial area (about 20-40 km downwind).

It is interesting to note that on some occasions (27 June, 3 July) ozone plumes were also observed from sources upwind of the Sarnia area (although on these days no impact on O_3 levels due to Sarnia emissions could be detected).

It should also be noted that during the June 27 - July 18 study period, flights were generally carried out only on days when there was some possibility of a Sarnia impact (with the exception of the Canada Day long weekend, when the study was suspended for three days). For example, several of the other 11 days during the above period were heavily overcast or rainy; however, on the Canada Day weekend meteorological conditions were favourable for local ozone formation. Thus, though it would not be justifiable to say that on only four days out of the total twenty-two in the study period was a Sarnia impact observed on the ozone levels in the area, one could reasonably say that, during the summer, such a measurable impact occurs about 30% of the time or less. A more accurate assessment of this figure could be carried out using long-term meteorological data for southwestern Ontario, together with the information on meteorological conditions leading to a Sarnia impact (Section 4.3).

4.2 Contribution of Sarnia vs. Long-range Transport to Regional O_3 Levels

A conclusive assessment of the Sarnia contribution to regional ozone levels is of course not possible on the basis of a three-week long field study, especially since the meteorological representativeness of the study period is open to question (see above). A parallel study of the long-term meteorological and ozone monitoring data in southwestern Ontario is currently underway as another component of MOE's oxidant strategy program, and will complement the present results. With this proviso in mind, the following facts can be considered:

(i) On the larger portion of the study days, no impact due to Sarnia emissions could be detected. These included one day (July 3) which approximated the classical "back-of-the-high pressure area" ozone episode, with ozone levels at most stations in the study area exceeding the provincial hourly air quality criterion of 80 ppb. This is not meant to imply that Sarnia hydrocarbon and NO_x emissions do not form atmospheric ozone. There are a number of hydrocarbons in the Sarnia emissions - for example, the alkyl benzenes - which are known to be efficient ozone precursors (Atkinson and Lloyd, 1984). However, during the few hours subsequent to emission that the polluted air parcel remained in the study area, chemical transformation rates and atmospheric dilution were such that measurable ozone buildups apparently did not occur.

(ii) On two days when a Sarnia impact was identified (July 13 and 14), and moreover regional ozone levels (as determined from upwind aircraft traverses and monitors clear of Sarnia emissions) were approaching the provincial air quality criterion, the additional ozone produced by Sarnia precursors caused the criterion to be exceeded. The area thus affected is estimated from the data in Figures 24 and 27 to be on the order of 100-1000 km^2, and the duration of the impact on the order of several hours (e.g. see Figure 26). (It may be noted for comparison that the area of southern Ontario, where exceedences of the provincial air quality criterion for ozone are frequently observed, is on the order of 100,000 km^2).

(iii) On the two other days when a Sarnia impact was identified, but regional ozone levels were well below the provincial air quality criterion - June 28 and July 8 - no exceedences of the criterion were observed (although on occasion, instantaneous levels in excess of 80 ppb were noted in the aircraft data).

On the basis of these limited observations, it can be concluded that the emissions from Sarnia can on occasion contribute to exceedences of the provincial air quality criterion over limited areas of southwestern Ontario, the affected areas being on the order of 100-1000 km^2 in size and occurring within a few tens of kilometers of the Sarnia industrial area.

However, on these occasions the maximum observed contributions from Sarnia were about 20-40 ppb above the "background"levels imported into the area, which were frequently well in excesss of 40 ppb. Bearing in mind the relatively infrequent occurrence of days when a Sarnia contribution can be detected, the magnitude of the observed contributions and the limited area affected, it is clear that ozone levels in southwestern Ontario are largely governed by the imported component, rather than generation from local emissions.

4.3 Meteorological Conditions Leading to a Sarnia Impact

With reference to the summary in Table 4, it can be seen that in general no Sarnia impact was observable on the days which were relatively overcast (27 June; 5, 7, 16, 17, 18 July), with temperatures generally (but not always) on the low side compared to the total set of days, and winds from the westerly quadrant. Air quality and atmospheric visibility in the area were good, because previously the air parcels had passed over areas with few sources of pollution. It is somewhat surprising that no Sarnia impact could be detected on July 3, since high ozone levels were observed in the study area, and an ozone plume had been apparently formed from emissions in the Windsor/Detroit area. The presence of scattered-to-broken clouds on this day, leading to inhibited irradiation, may be of significance. A few more samples of this type of "back-of-the-high" day in the present study would have been very useful.

On the other hand, ozone buildups attributable to Sarnia were observed on several days (8, 13, 14 July) with relatively clear skies and light winds, especially in the morning, when a brown haze layer was noted over the Sarnia area. Temperatures tended to be on the high side compared to the total set of study days, and the atmosphere was somewhat more stable, especially in the morning when low mixing heights were observed (- note, however, that relatively low mixing heights also occurred on several days in Table 4 when there was no detectable Sarnia impact on ozone levels). A variety of previous air mass histories was noted, including travel over upwind areas of both low and high emission densities, and this fact was reflected in the overall air quality in the area (e.g. compare July 8, which had good regional air quality and atmospheric visibility, with July 14, when conditions were much more marginal). An exception to the above picture in several respects is 28 June, when fairly brisk westerly winds were encountered, there was no evidence of an early morning stagnation period, and the mixing layer was quite deep (up to 2000 m). Background air quality was generally good in the study area. Apart from the fact that skies were clear on this day, it is similar in many respects to days in the "no-Sarnia-impact" category (which were overcast), so insolation is evidently an important variable in determining whether or not there will be an impact due to local ozone precursor emissions (- note also the comparison in Section 3.4 of July 5, 8 and 13).

In a recent paper, Kelly et al. (1985) have presented an extensive discussion of the meteorological conditions associated with ozone buildups in the Detroit Metropolitan area. Since the geographical area here is basically the same as in Kelly et al.'s paper, and Kelly's analysis is based on a relatively large data set, it is interesting to compare the present study's results with the conclusions of Kelly et al. On the basis of a comparison of meteorology and air quality on upper versus lower quartile ozone days, they found that the high ozone days tended to be warmer and sunnier, and had higher barometric pressure and lower wind speeds. Mixing was inhibited on these days, and considerably higher morning pollutant concentrations were noted (in the Detroit Metropolitan area). Strictly speaking, in the above analysis Kelly et al. were not considering the contribution from any specific source area (as in the present study), but rather the total ozone level measured due to a number of upwind contributions. However, their comments are directly relevant as far as the potential for ozone formation from its precursor emissions is concerned, since the upper quartile days are expected to also have a high ozone formation potential. The above meteorological description (Kelly et al., 1985) applies fairly well to 8, 13 and 14 July, when a Sarnia contribution was detected, and one can justifiably generalize that if such conditions occur in southwestern Ontario, then ozone buildups due to Sarnia emissions are highly probable. However, there are other days, such as 28 June, when a Sarnia contribution was also detected, which had clean background air, and even with the Sarnia contribution included, air quality in the study area was good.

4.4 Atmospheric Chemistry and the Impact of Sarnia Emissions

As was already noted in the Introduction, a detailed consideration of the atmospheric chemistry, and the question of hydrocarbon v.s. NO_x control in the Sarnia area, is beyond the scope of this report. These will be dealt with elsewhere. However, some relevant observations can be made, based on an examination of data collected on the aircraft sampling days.

Firstly, it is interesting to note that, with the exception of June 28 (when the overall air quality in the area was good), hydrocarbon and NO_x levels were relatively high on days when a Sarnia impact on regional ozone was noted, especially in the morning (- it must be pointed out, however, that on some other days - 5 and 17 July - when hydrocarbon and NO_x levels were also high, no ozone buildup downwind of Sarnia was detected, presumably because of lack of sunlight to drive the atmospheric photochemistry). On a number of occasions, significant amounts of alkenes and alkylbenzenes, which are recognized to be ozone precursors, were noted downwind of Sarnia. On 8 July, the aircraft data suggested that the alkylbenzenes may be especially important as far as ozone formation in the Sarnia plume is concerned, but this result must be regarded with caution, since several of the aircraft hydrocarbon samples were suspected to be contaminated. On several occasions elevated levels of aliphatics, which can also form ozone (but on longer time scales - Atkinson and Lloyd, 1984 - and hence not within the study area), were found downwind of Sarnia.

The ozone precursor monitors in general gave high readings when concurrent hydrocarbon and NO_x levels were high, and low readings when they were also low. An interpretation of the ozone precursor monitor results, regarding the question of whether hydrocarbons or nitrogen oxides are the more important ozone precursor in southwestern Ontario, is made difficult by the fact that much of the time NO_x levels were below instrumental detection limits. There is some circumstantial evidence in the data to suggest that in the Sarnia area, oxidant formation may be NO_x -limited (- see the discussion of the July 14 data, Section 3.8, for example). However, this is contradicted by some of the other data (e.g., on 8 July), which suggest that hydrocarbons may play an important role. A resolution to this question will have to await a more detailed analysis of the data (particularly at the Camlachie site, where the high-sensitivity NO_x analyser was located), as well as the results of the planned mathematical modelling scenario runs.

Table 4: Summary of Sarnia Oxidant Study Observations

Date/Time	O_3 Observations		Meteorology	NO_x, HC, O_3 Precursor Monitor Observations	Other
	Sarnia Impact	Regional O_3			
27 June 1300-1700 EDT	No, but there was some evidence for an O_3 plume from a source upwind of Sarnia	30-50 ppb	- overcast - brisk W'ly winds (25-36 km h^{-1}) - temp. in mid - 20's - rel. hum. about 60% - mixing ht. greater than 1000 m - air back trajectories from Nebraska northeastwards to Sarnia	- generally good air quality throughout the day	- upwind $SO_4 = 12$ ug m^{-3} $NO_3 = 1$ ug m^{-3} $b_{scat} = 1 \times 10^{-4}$ m^{-1}
28 June 0900 - 1300 EDT	Yes, there was evidence for a downwind plume. The data suggest a delay in O_3 formation, no buildup being detected within the first hour or so of air parcel travel time.	30-40 ppb	- clear - W'ly winds (5-20 km h^{-1}) - temp. low to mid- 20's - rel. hum. about 50% - max. rad. 94 mw cm^{-2} - mixing ht. 600 to 2000 m - air back trajectories from west edge of Lake Superior, south eastward to central Lake Michigan, then westward to Sarnia	- no early morning buildup of HC, NO_x - downwind of Sarnia, HC's were at or below overall survey levels, NO_x generally below detection limits - no downwind O_3 precursor monitor measurements were available	- upwind $SO_4 = 12$ ug m^{-3} $NO_3 = 2$ ug m^{-3} $b_{scat} = 1 \times 10^{-4}$ m^{-1} H_2O_2 about 2 ppb
3 July 1000 - 1800 EDT	No, but an O_3 plume apparently from the Windsor-Detroit area was observed.	Greater than 80 ppb in afternoon.	- back-of-high pressure system - SW winds (10-20 km h^{-1}) - temp. mid-to upper 20's - scattered/broken clouds - rel. hum. about 50% - max. rad. 101 mw cm^{-2} - mixing ht. greater than 1000 m - air back trajectories follow a northeastward path from Indiana and Illinois	- no early morning HC or NO_x buildup, but relatively high levels of alkanes and aromatics at Camlachie, downwind of Sarnia - no O_3 precursor monitor measurements available downwind of Sarnia	- upwind $SO_4 = 64$ ug m^{-3} $NO_3 = 15$ ug m^{-3} b_{scat} greater than 2×10^{-4} m^{-1}

Table 4: **Summary of Sarnia Oxidant Study Observations** (Cont'd)

Date/Time	O_3 Observations		Meteorology	NO_x, HC, O_3 Precursor Monitor Observations	Other
	Sarnia Impact	Regional O_3			
5 July 0900-1300 EDT	No	Generally less than 60 ppb.	- broken to overcast cloud cover - light and variable winds - temp. near 20^{o}C - rel. hum. 60-70% - max. rad. 70 mw cm^{-2} - mixing ht. 200-500 m - air back trajectories from Illinois, northeastward to lower Lake Michigan, then eastward to Sarnia	- generally high HC's (mainly alkanes and aromatics) - O_3 precursor monitor levels up to 16 ppb	- upwind SO_4 = 75 ug m^{-3} NO_3 = 8 ug m^{-3} (possibly due to an imported plume)
7 July 0900-1400 EDT	No	Less than 40 ppb.	- cloudy - W - NW winds (20-25 km h^{-1}) - temp. 13 - 18^{o}C - rel. hum. 50-60% - max. rad. 60 mw cm^{-2} - morning mixing layers at less than 700 m, stable in afternoon - air back trajectories from North Ontario	- low HC, NO_x levels throughout the area - O_3 precursor analyser measurements below detection limits	- upwind SO_4 = 6 ug m^{-3} NO_3 = 0.8 ug m^{-3} b_{scat} less than 0.5 x 10^{-4} m^{-1}
8 July 0800-1900 EDT	Pockets of elevated O_3 concentrations in morning. Relatively high O_3 observed at some intermediate ground-level sites in afternoon.	Less than 30 ppb in morning. About 40 ppb in afternoon.	- clear - light and variable winds - lake breeze in afternoon - temp. low to mid-20's - rel. hum. 40-50% - max. rad. 100 mw cm^{-2} - mixing ht. between 150 and 800 m throughout day - air back trajectories from west Lake Superior, southeastward across central Lake Michigan	- relatively high early morning NO_x, HC (alkanes, benzene, alkylbezenes) levels - however, O_3 precursor data were found to be low - aircraft HC data suggest that alkylbenzenes may be an important O_3 precursor	- brown haze in morning over Sarnia - upwind SO_4 = 6 ug m^{-3} NO_3 = 2 ug m^{-3} b_{scat} less than 0.5 x 10^{-4} m^{-1}

Table 4: Summary of Sarnia Oxidant Study Observations (Cont'd)

Date/Time	O_3 Observations		Meteorology	NO_x, HC, O_3 Precursor Monitor Observations	Other
	Sarnia Impact	Regional O_3			
13 July 0800-1700 EDT	Yes, there was evidence for a downwind O_3 plume, with maximum concentrations about 20-40 km from Sarnia.	30-40 ppb in morning. 50-70 ppb in afternoon.	- relatively clear - light winds (5-15 km h^{-1}) - lake breeze - temp. in mid-upper 20's - rel. hum. 50-60% - max. rad. 103 mw cm^{-2} - mixing ht. 100 to 1000 m in morning - air back trajectories from west Wisconsin, southeast and central Lake Michigan	- NO_x, HC (alkanes, alkylbezenes) relatively high in early morning - relatively high O_3 precursor monitor values (20 ppb)	- brown haze in morning over Sarnia - upwind SO_4 = 6 ug m^{-3} NO_3 = 2 ug m^{-3} b_{scat} less than 1×10^{-4} m^{-1}
14 July 0900-1200 EDT	A Sarnia impact is suggested in the aircraft and ground level data.	Rapidly increasing in morning. Greater than 80 ppb at most stations by late p.m. Large O_3 reservoir aloft during morning.	- scattered clouds - southwesterly winds (10-20 km h^{-1}) - temp. in mid-upper 20's - rel. hum. 50-60% - max. rad. 80 mw cm^{-2} - morning mixing ht. 150 to 1000 m - air back trajectories from Illinois northeastward	- relatively high morning levels of alkenes, aromatics at Courtright, Camlachie - urban HC and NO_x levels were not abnormal - relatively high O_3 precursor monitor values (up to 27 ppb)	- brown haze in morning over Sarnia - upwind SO_4 = 54 ug m^{-3} NO_3 = 20 ug m^{-3} b_{scat} greater than 1×10^{-4} m^{-1}
16 July 0800-1300 EDT	No	Less than 45 ppb.	- broken clouds - W - NW winds (20-25 km h^{-1}) - temp. low 20's - rel. hum. 50-60% - max. rad. 100 mw cm^{-2} - mixing ht. 400 - 600 m - air back trajectories from Manitoba southeastwards	- relatively low HC, NO_x levels - O_3 precursor levels below detection limits	- upwind SO_4 = 4 ug m^{-3} NO_3 = 1 ug m^{-3} b_{scat} less than 0.5×10^{-4} m^{-1}

Table 4: **Summary of Sarnia Oxidant Study Observations** (Cont'd)

Date/Time	O_3 Observations		Meteorology	NO_x, HC, O_3 Precursor Monitor Observations	Other
	Sarnia Impact	Regional O_3			
17 July 0800-1100 EDT	No	Less than 60 ppb (daily max).	- overcast - SW'ly winds (15-20 km h^{-1}) - temp. low 20's - rel. hum. 60-70% - rad. at time of flight 30 mw cm^{-2} - mix. ht. zero to 500 m - air back trajectories from north Michigan, to lower Lake Michigan, then NE to Sarnia	- relatively high HC, NO_x, due to low mixing height at time of sampling - O_3 precursor monitor at 11-20 ppb	- upwind $b_{scat} = 0.5 - 1.0 \times 10^{-4}\ m^{-1}$ - no SO_4, NO_3 data
18 July 1100-1300 EDT	No	Less than 45 ppb.	- overcast - NW'ly winds (20 km h^{-1}) - temp. in upper teens - rel. hum. 60-80% - rad. 60-80 mw cm^{-2} - mix. ht. 400-800 m - air back trajectories from central Minnesota through Lake Michigan and SE to Sarnia	- relatively low HC, NO_x levels - O_3 precursor monitor levels below detection limits	- upwind $SO_4 = 17\ ug\ m^{-3}$ $NO_3 = 2\ ug\ m^{-3}$ $b_{scat} = 0.5 \times 10^{-4} m^{-1}$

5. Conclusions

The conclusions below are based on a relatively small data set, which may not be entirely representative of the long-term situation. However, they seem to be consistent with the findings of other investigators who have studied the formation of ozone downwind of urban and industrial areas (see Kelly et al., 1985, as well as the references cited in the Introduction of this report).

(i) Oxidant precursor emissions from the Sarnia area can lead to the formation of elevated ozone levels downwind. This was observed to occur on four days in the June 27 - July 18 period, out of the eleven days when aircraft flights were carried out. The data suggest that local emissions lead to elevated downwind ozone levels on sunny summer days, especially those with low wind speeds and inhibited atmospheric mixing.

(ii) On these occasions, maximum ozone buildups (above regional background levels) of about 20-40 ppb can be observed. The affected areas can be on the order of 100-1000 km^2 in size, and the duration of the impact - several hours. At times, the Sarnia contribution to the total oxidant levels can push hourly ozone concentrations over the provincial air quality criterion of 80 ppb.

(iii) Nevertheless, judging from the frequency of occurrence of ozone buildups attributable to Sarnia emissions, the size of the area affected, and the magnitude of the Sarnia contributions compared to the regional background values, it is clear that ozone levels in southwestern Ontario in the summer are largely governed by the imported component, rather than generation from local emissions. A more quantitative assessment of Sarnia's contribution, based on a meteorological analysis of the long-term air monitoring data in the area, is currently in progress.

(iv) A large number of hydrocarbons known to be ozone precursors - especially the alkylated benzenes - can be detected in the air in the Sarnia area, presumably from emissions at a number of petrochemical industries at Sarnia. Although hydrocarbon levels were found to be generally higher on mornings of days when a Sarnia impact was detected in the ozone measurements, it is at present not possible to deduce whether local control measures (should they be necessary) should concentrate on hydrocarbon or NO_x reductions. This is the subject of an ongoing analysis of the air quality measurements, as well as mathematical modelling simulations.

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